

## Cycloadditions of Oxacyclic Allenes and a Catalytic Asymmetric Entryway to Enantioenriched Cyclic Allenes

Michael M. Yamano,<sup>†</sup> Rachel R. Knapp,<sup>†</sup> Aurapat Ngamnithiporn,<sup>‡</sup> Melissa Ramirez,<sup>†</sup>  
K. N. Houk,<sup>\*,†</sup> Brian M. Stoltz,<sup>\*,‡</sup> and Neil K. Garg<sup>\*,†</sup>

<sup>†</sup> Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095, United States

<sup>‡</sup> The Warren and Katharine Schlinger Laboratory of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

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## Part I. Experimental Section.

**Materials and Methods.** Unless stated otherwise, reactions were conducted in flame-dried glassware under an atmosphere of nitrogen using anhydrous solvents (freshly distilled or passed through activated alumina columns). All commercially obtained reagents were used as received unless otherwise specified. Cesium fluoride (CsF), tetrakis(triphenylphosphine)palladium(0) ( $\text{Pd}(\text{PPh}_3)_4$ ), and tris(dibenzylideneacetone)dipalladium(0) ( $\text{Pd}_2(\text{dba})_3$ ) were obtained from Strem Chemicals. (1,3)-diphenylisobenzofuran (**21**), *N*-*tert*-butyl- $\alpha$ -phenylnitrone (**SI-3**), chlorotrimethylsilane (TMSCl) were obtained from Alfa Aesar. *N*-(5-chloro-2-pyridyl)bis(trifluoromethanesulfonimide) (Comins' Reagent), *n*-butyllithium (*n*-BuLi), potassium bis(trimethylsilyl)amide (KHMDs), *N*-Boc pyrrole (**17**), *N*-phenylpyrrole (**15**), 2,5-dimethylfuran (**19**), dicyclopentadiene, dimethylphenylsilyl chloride ( $\text{PhMe}_2\text{SiCl}$ ), and allyl chloroformate were obtained from Sigma Aldrich. Diisopropylamine and 1,4-diazabicyclo[2.2.2]octane (DABCO) were obtained from Acros Organics. Indene (**43**) was purchased from Combi-Blocks. (**19**), TMSCl, and diisopropylamine were distilled over  $\text{CaH}_2$  prior to use. Allyl chloroformate was dessicated with  $\text{CaCl}_2$  and distilled prior to use. **17** was filtered over basic alumina prior to use. Dicyclopentadiene was cracked and cyclopentadiene (**23**) was stored at  $-80^\circ\text{C}$  prior to use. Reaction temperatures were controlled using an IKA Mag temperature modulator and, unless stated otherwise, reactions were performed at room temperature (approximately  $23^\circ\text{C}$ ). Thin layer chromatography (TLC) was conducted with EMD gel 60 F254 pre-coated plates (0.25 mm) and visualized using a combination of UV light, anisaldehyde, and potassium permanganate staining. Silicycle Siliashield P60 (particle size 0.040–0.063 mm) was used for flash column chromatography.  $^1\text{H}$ -NMR and 2D-NOESY spectra were recorded on Bruker spectrometers (at 300, 400, 500, and 600 MHz) and are reported relative to the residual solvent signal. Data for  $^1\text{H}$ -NMR spectra are reported as follows: chemical shift ( $\delta$  ppm), multiplicity, coupling constant (Hz) and integration.  $^{13}\text{C}$ -NMR spectra were recorded on Bruker spectrometers (at 100 and 125 MHz) and are reported relative to the residual solvent signal. Data for  $^{13}\text{C}$ -NMR spectra are reported in terms of chemical shift and, when necessary, multiplicity, and coupling constant (Hz).  $^{19}\text{F}$  NMR spectra were recorded on Bruker spectrometers (at 376 MHz) and reported in terms of chemical shift ( $\delta$  ppm). IR spectra were obtained on a Perkin-Elmer UATR Two FT-IR spectrometer and are reported in terms of frequency of absorption ( $\text{cm}^{-1}$ ). Uncorrected melting points were measured using a DigiMelt

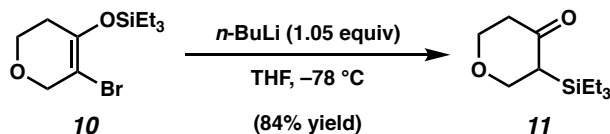


MPA160 melting point apparatus. DART-MS spectra were collected on a Thermo Exactive Plus MSD (Thermo Scientific) equipped with an ID-CUBE ion source and a Vapor Interface (IonSense Inc.). Both the source and MSD were controlled by Excalibur software v. 3.0. The analyte was spotted onto OpenSpot sampling cards (IonSense Inc.) using CDCl<sub>3</sub> as the solvent. Ionization was accomplished using UHP He (Airgas Inc.) plasma with no additional ionization agents. The mass calibration was carried out using Pierce LTQ Velos ESI (+) and (–) Ion calibration solutions (Thermo Fisher Scientific). Determination of enantiopurity was carried out on a Mettler Toledo SFC (supercritical fluid chromatography) using a Daicel ChiralPak IC-3 column and a Daicel ChiralPak AD-3 column. Optical rotations were measured with a Rudolph Autopol III Automatic Polarimeter.

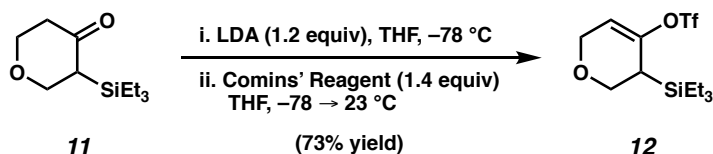
Nitrones **SI-2**,<sup>1</sup> **54**,<sup>2</sup> **SI-4**, **SI-5**,<sup>3</sup> **SI-6**,<sup>4</sup> **SI-7**,<sup>4</sup> **SI-8**,<sup>3</sup> azomethine imines **37**<sup>5</sup> and **39**,<sup>6</sup> nitrile oxide **41**,<sup>7</sup> imidazole carboxylate **SI-14**,<sup>8</sup> and (*S*)-(CF<sub>3</sub>)<sub>3</sub>-*t*-BuPHOX (**47**)<sup>9</sup> are all known compounds. <sup>1</sup>H-NMR spectral data matched those reported in the literature.

## Experimental Procedures.

### A. Synthesis of Silyl Triflate 12.



**Silyl ketone 11.** To a solution of known silyl enol ether **10**<sup>10</sup> (5.6 g, 19.1 mmol, 1.0 equiv) in THF (225 mL) at  $-78\text{ }^{\circ}\text{C}$  was added *n*-BuLi (2.02 M in hexanes, 9.9 mL, 20.1 mmol, 1.05 equiv) dropwise over 18 min. The solution was stirred for 43 min at  $-78\text{ }^{\circ}\text{C}$ , then the reaction was quenched with sat. aq.  $\text{NaHCO}_3$  (80 mL) and allowed to warm to  $23\text{ }^{\circ}\text{C}$ . The layers were then separated and the aqueous layer was extracted with EtOAc (3 x 80 mL). The combined organic layers were then dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The resulting crude oil was purified by flash chromatography (19:1 hexanes:EtOAc) to afford silyl ketone **11** (3.4 g, 84% yield) as a colorless oil. Silyl ketone **11**:  $R_f$  0.29 (9:1 hexanes:EtOAc);  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.20–4.09 (m, 2H), 3.92 (dd,  $J = 11.4, 4.6$ , 1H), 3.74 (ddd,  $J = 11.4, 10.9, 4.0$ , 1H), 2.47 (ddd,  $J = 15.6, 10.9, 6.8$ , 1H), 2.38–2.31 (m, 2H), 0.97 (t,  $J = 7.7$ , 9H), 0.68 (q,  $J = 7.7$ , 6H);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  207.7, 68.1, 67.2, 44.5, 42.0, 7.4, 3.2; IR (film): 2954, 2911, 2876, 1691, 1218  $\text{cm}^{-1}$ ; HRMS–APCI ( $m/z$ )  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{11}\text{H}_{23}\text{O}_2\text{Si}^+$ , 215.14618; found, 215.14678.

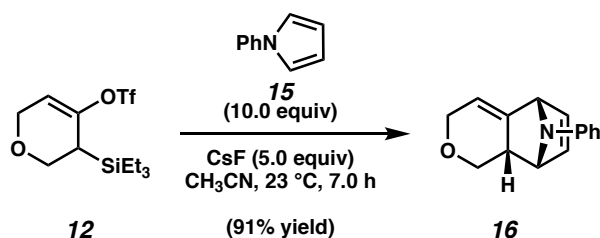


**Silyl triflate 12.** To a solution of diisopropylamine (1.30 mL, 9.1 mmol, 1.30 equiv) in THF (8.0 mL) at  $-78\text{ }^{\circ}\text{C}$  was added *n*-BuLi (2.02M in hexanes, 4.20 mL, 8.4 mmol, 1.20 equiv) dropwise over 7 min. The reaction was then stirred at  $-78\text{ }^{\circ}\text{C}$  for 20 min and then allowed to warm to  $23\text{ }^{\circ}\text{C}$ . After stirring for 10 min at  $23\text{ }^{\circ}\text{C}$ , the reaction mixture was again cooled to  $-78\text{ }^{\circ}\text{C}$  and a solution of silyl ketone **11** (1.5 g, 7.01 mmol, 1.0 equiv) in THF (8.0 mL) was added dropwise over 15 min and left to stir for 1.0 h at  $-78\text{ }^{\circ}\text{C}$ . A solution of Comins' Reagent (3.86 g, 9.81 mmol, 1.4 equiv) in THF (8.2 mL) was then added dropwise over 20 min at  $-78\text{ }^{\circ}\text{C}$ . The reaction was then stirred for 10 min at  $-78\text{ }^{\circ}\text{C}$  before being warmed to  $23\text{ }^{\circ}\text{C}$ . After stirring for an additional 14 h, the reaction mixture was quenched by the addition of sat. aq.  $\text{NaHCO}_3$  (30 mL),

and the layers were separated. The aqueous layer was extracted with Et<sub>2</sub>O (3 x 30 mL) and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The resulting crude oil was purified by flash chromatography (4:1 hexanes:benzene) to give silyl triflate **12** (1.77 g, 73% yield) as a colorless oil. Silyl triflate **12**: *R<sub>f</sub>* 0.55 (9:1 hexanes:EtOAc); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 5.67–5.65 (m, 1H), 4.25 (qt, *J* = 16.1, 3.1, 2H), 3.96 (dd, *J* = 11.2, 4.7, 1H), 3.86 (dd, *J* = 11.2, 4.7, 1H), 2.14–2.10 (m, 1H), 0.98 (t, *J* = 8.2, 9H), 0.68 (q, *J* = 8.0, 6H); <sup>13</sup>C-NMR (125 MHz): δ 149.7, 118.7 (q, *J* = 318.3), 113.0, 66.7, 64.4, 28.5, 7.3, 2.9; <sup>19</sup>F-NMR (376 Hz, CDCl<sub>3</sub>): –73.5; IR (film): 2957, 2880, 1681, 1418, 1245, 1207 cm<sup>–1</sup>; HRMS–APCI (*m/z*) [*M* + *H*]<sup>+</sup> calcd for C<sub>12</sub>H<sub>22</sub>F<sub>3</sub>O<sub>4</sub>Si<sup>+</sup>, 347.09547; found, 347.09659

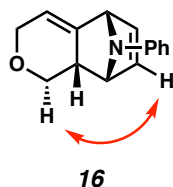
## B. Diels–Alder Trapping Experiments.

**Representative Procedure (Preparation of cycloadduct **16** is used as an example).**

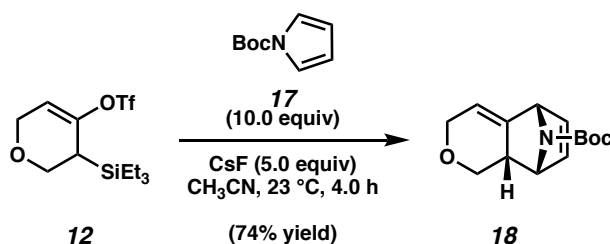


**Cycloadduct **16**.** To a stirred solution of silyl triflate **12** (52.6 mg, 0.152 mmol, 1.0 equiv) and *N*-phenylpyrrole (**15**, 217 mg, 1.52 mmol, 10.0 equiv) in CH<sub>3</sub>CN (1.52 mL) was added CsF (115.0 mg, 0.759 mmol, 5.0 equiv). The reaction vessel was sealed with a PTFE lined cap and allowed to stir at 23 °C for 7 h. The crude reaction mixture was then filtered by passage through a plug of silica gel (EtOAc eluent, 10 mL). Concentration under reduced pressure yielded the crude residue (3.8:1 dr, average of two experiments). Purification by preparative thin layer chromatography (5:1 hexanes:EtOAc) allowed for separation of the two diastereomers, which were obtained in a total yield of 91% (average of two experiments). The major diastereomer **16** was obtained as a light yellow amorphous solid. Cycloadduct **16**: *R<sub>f</sub>* 0.15 (5:1 hexanes:EtOAc); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 7.23–7.18 (m, 2H), 6.87–6.80 (m, 3H), 6.30 (dd, *J* = 5.6, 2.6, 1H), 5.97 (dd, *J* = 5.7, 2.1, 1H), 5.69–5.68 (m, 1H), 4.89 (br s, 1H), 4.71–4.70 (m, 1H), 4.25 (dt, *J* = 16.5, 2.1, 1H), 4.15 (dd, *J* = 9.4, 4.7, 1H), 3.96 (dt, *J* = 16.6, 3.0, 1H), 2.64–2.60 (m, 1H), 2.46 (t, *J* = 9.8, 1H); <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>): δ 146.8, 137.6, 135.0, 129.2, 128.4, 120.7, 117.7, 117.3, 67.9, 65.4, 64.96, 64.95, 38.6; IR (film): 3060, 3005, 2920, 1496, 1315 cm<sup>–1</sup>; HRMS–APCI (*m/z*) [*M* + *H*]<sup>+</sup> calcd for C<sub>15</sub>H<sub>16</sub>NO<sup>+</sup>, 226.12264; found, 226.12161.

The structure of **16** was verified by 2D-NOESY, as the following interaction was observed:



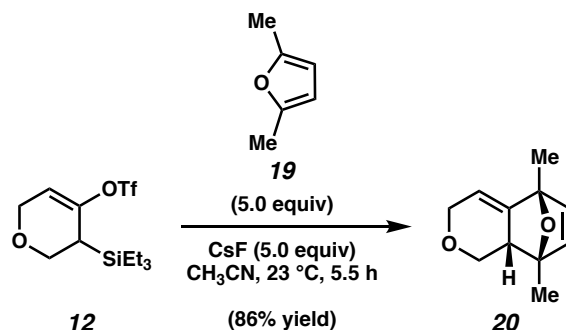
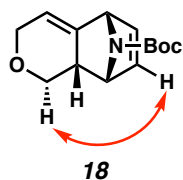
All reactions were monitored by TLC until starting material was consumed; the specific times are listed in the reaction scheme for each reaction. Any modifications of the conditions shown in this representative procedure are specified in the following schemes, which depict all of the results shown in Table 1. For all compounds in which the diastereomeric ratios were >20:1, the minor diastereomer was not observed in the  $^1\text{H}$ -NMR spectrum of the crude reaction mixture.



**Cycloadduct 18.** Following concentration under reduced pressure, the crude residue was obtained (6.2:1 dr, average of two experiments). Purification by preparative thin layer chromatography (5:1 hexanes:Et<sub>2</sub>O) allowed for separation of the two diastereomers, which provided a total yield of 74% (average of two experiments). Major diastereomer **18** was obtained as a clear oil. Cycloadduct **18**:  $R_f$  0.28 (9:1 hexanes:EtOAc);  $^1\text{H}$ -NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  6.32 (br s, 1H), 5.99–5.95 (m, 1H), 5.61 (br s, 1H), 4.99–4.93 (m, 1H), 4.79–4.73 (m, 1H), 4.28 (dt,  $J$  = 16.6, 2.1, 1H), 4.14 (dd,  $J$  = 9.6, 4.8, 1H), 3.95 (dt,  $J$  = 16.6, 2.9, 1H), 2.65 (br s, 1H), 2.36 (t,  $J$  = 10.1, 1H), 1.43 (s, 9H);  $^{13}\text{C}$ -NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  155.1, 136.3, 135.5, 129.5, 128.3, 120.2, 117.0, 116.4, 80.6, 67.6, 65.0, 63.7, 63.0, 62.1, 61.6, 39.8, 39.3, 28.4; IR (film): 2978, 1738, 1599, 1319, 1160 cm<sup>-1</sup>; HRMS–APCI ( $m/z$ ) [ $M + H$ ]<sup>+</sup> calcd for C<sub>14</sub>H<sub>20</sub>NO<sub>3</sub><sup>+</sup>, 250.14377; found, 250.14536.

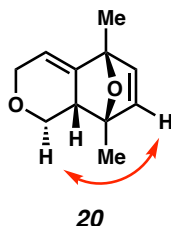
*Note: 18 was obtained as a mixture of rotamers. These data represent empirically observed chemical shifts from the  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra.*

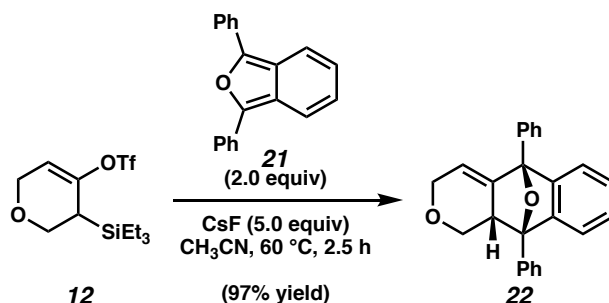
The structure of **18** was verified by 2D-NOESY, as the following interaction was observed:



**Cycloadduct 20.** Following concentration under reduced pressure, the crude residue was obtained (9.2:1 dr, average of two experiments). Purification by flash chromatography (5:1 pentanes:Et<sub>2</sub>O) allowed for separation of the two diastereomers, which afforded a total yield of 86% (average of two experiments). Major diastereomer **20** was obtained as a colorless oil. Cycloadduct **20**: *R<sub>f</sub>* 0.27 (9:1 hexanes:EtOAc); <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): δ 6.13 (d, *J* = 5.4, 1H), 5.82 (d, *J* = 5.4, 1H), 5.48 (app q, *J* = 2.3, 1H), 4.28 (dt, *J* = 16.5, 2.1, 1H), 4.11 (dd, *J* = 9.3, 4.7, 1H), 3.94 (dt, *J* = 16.4, 2.9, 1H), 2.45–2.41 (m, 1H), 2.36–2.32 (m, 1H), 1.63 (s, 3H), 1.62 (s, 3H); <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>): δ 143.5, 139.9, 132.8, 113.7, 86.8, 86.6, 67.2, 64.6, 46.5, 18.2, 14.8; IR (film): 2973, 2929, 2851, 1382, 1308 cm<sup>−1</sup>; HRMS–APCI (*m/z*) [*M* + *H*]<sup>+</sup> calcd for C<sub>11</sub>H<sub>14</sub>O<sub>2</sub><sup>+</sup>, 179.10666; found, 179.10719.

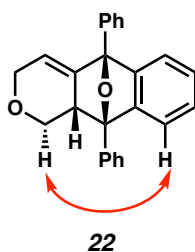
The structure of **20** was verified by 2D-NOESY, as the following interaction was observed:

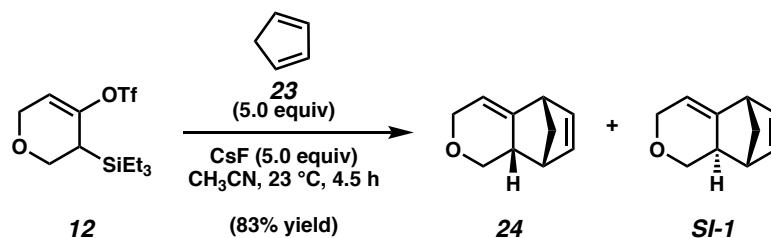




**Cycloadduct 22.** Following concentration under reduced pressure, the crude residue was obtained (2.0:1 dr, average of two experiments). Purification by preparative thin layer chromatography (9:1 hexanes:EtOAc) allowed for separation of the two diastereomers, which provided a total yield of 97% (average of two experiments). Major diastereomer **22** was obtained as a clear oil. Cycloadduct **22**:  $R_f$  0.36 (9:1 hexanes:EtOAc);  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.88–7.86 (m, 2H), 7.65–7.63 (m, 2H), 7.53–7.45 (m, 5H), 7.43–7.41 (m, 1H), 7.25–7.21 (m, 2H), 7.17–7.14 (m, 1H), 7.01–6.99 (m, 1H), 5.71 (app q,  $J = 2.5$ , 1H), 4.45 (dd,  $J = 9.8, 4.9$ , 1H), 4.34 (dt,  $J = 16.9, 2.5$ , 1H), 3.87 (ddd,  $J = 16.6, 3.6, 2.9$ , 1H), 3.43–3.39 (m, 1H), 2.40 (t,  $J = 10.2$ , 1H);  $^{13}\text{C-NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  148.1, 144.3, 142.5, 137.3, 134.1, 129.0, 128.72, 128.66, 128.6, 128.5, 127.6, 127.0, 126.4, 121.3, 118.6, 118.0, 90.2, 89.4, 67.0, 64.9, 46.3; IR (film): 3060, 2923, 1734, 1448, 734  $\text{cm}^{-1}$ ; HRMS–APCI ( $m/z$ )  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{25}\text{H}_{21}\text{O}_2^+$ , 353.15361; found, 353.15563.

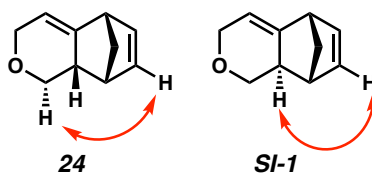
The structure of **22** was verified by 2D-NOESY, as the following interaction was observed:

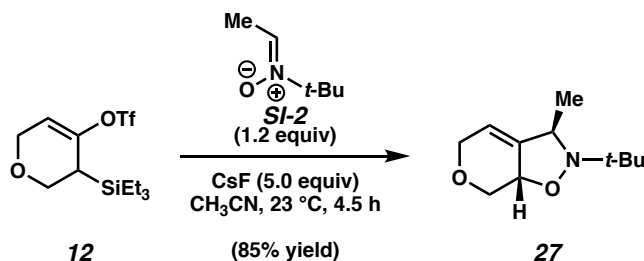




**Cycloadducts 24 and SI-1.** Following concentration under reduced pressure, the crude residue was obtained (1.6:1 dr, average of two experiments). Purification by flash chromatography (30:1 pentane:Et<sub>2</sub>O), provided a total yield of 83% (average of two experiments) of **24** and **SI-1** as an inseparable mixture. **24** and **SI-1** (inseparable mixture) were obtained as a colorless oil. Cycloadducts **24** and **SI-1**: *R<sub>f</sub>* 0.62 (9:1 hexanes:EtOAc); <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ 6.34 (dd, *J* = 5.7, 3.1, 1H, **SI-1**), 6.09–6.02 (m, 1H, **24**, 1H, **SI-1**), 5.77 (dd, *J* = 5.5, 2.9, 1H, **24**), 5.59–5.54 (m, 1H, **SI-1**), 5.48–5.44 (m, 1H, **24**), 4.29 (dt, *J* = 15.9, 2.0, 1H, **SI-1**), 4.26 (dt, *J* = 16.4, 2.2, 1H, **24**), 4.15–4.06 (m, 1H, **24**, 2H, **SI-1**), 3.97 (dt, *J* = 16.9, 2.9, 1H, **24**), 3.36 (br s, 1H, **SI-1**), 3.26 (br s, 1H, **24**), 2.99 (dd, *J* = 10.6, 9.6, 1H, **SI-1**), 2.95–2.90 (m, 1H, **24**), 2.70 (br s, 1H, **SI-1**), 2.54–2.45 (m, 1H, **24**), 2.41 (dd, *J* = 10.2, 8.7, 1H, **24**), 2.02–1.92 (m, 1H, **SI-1**), 1.63 (dt, *J* = 8.2, 1.6, 1H, **24**), 1.59–1.54 (m, 1H, **SI-1**), 1.52–1.47 (m, 1H, **24**), 1.41–1.37 (m, 1H, **SI-1**); <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>): δ 142.6, 141.3, 138.7, 136.2, 132.8, 129.8, 114.9, 114.4, 69.0, 67.8, 65.2 (2C), 50.0, 49.1, 48.7, 47.4, 43.5, 41.9, 41.2, 40.9; IR (film): 3059, 2970, 2924, 2851, 1375 cm<sup>-1</sup>; HRMS–APCI (*m/z*) [*M* + *H*]<sup>+</sup> calcd for C<sub>10</sub>H<sub>13</sub>O<sup>+</sup>, 149.09609; found, 149.09597.

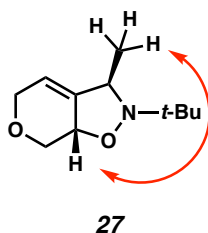
The structures of **24** and **SI-1** were verified by 2D-NOESY, as the following interaction were observed:



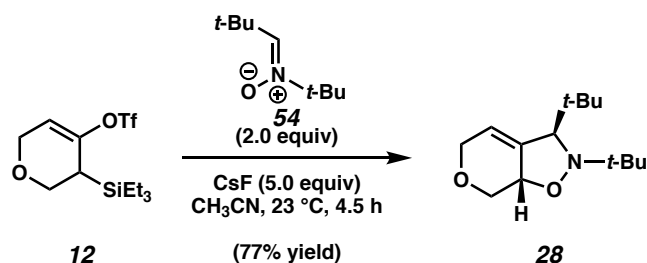
**C. (3+2) Trappings with Nitrones.****Representative Procedure (Preparation of isoxazolidine **27** is used as an example).**

**Isoxazolidine 27.** To a stirred solution of silyl triflate **12** (52.2 mg, 0.151 mmol, 1.0 equiv) and nitron **SI-2** (20.8 mg, 0.181 mmol, 1.2 equiv) in  $\text{CH}_3\text{CN}$  (1.51 mL) was added **CsF** (114 mg, 0.753 mmol, 5.0 equiv). The reaction vessel was sealed with a PTFE lined cap and allowed to stir at 23 °C for 4.5 h. The reaction mixture was filtered by passage through a plug of silica gel (EtOAc eluent, 10 mL). Concentration under reduced pressure yielded the crude residue (>20:1 dr, average of two experiments). Purification by preparative thin layer chromatography (5:1 hexanes:EtOAc) afforded isoxazolidine **27** as a clear, colorless oil (85% yield, average of two experiments). Isoxazolidine **27**:  $R_f$  0.25 (9:1 hexanes:EtOAc);  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.46–5.45 (m, 1H), 4.38–4.34 (m, 1H), 4.27 (dd,  $J$  = 10.1, 5.9, 1H), 4.16 (dq,  $J$  = 16.3, 2.4, 1H), 4.07–4.01 (m, 1H), 3.74–3.70 (m, 1H), 3.11 (app t,  $J$  = 8.9, 1H), 1.29 (d,  $J$  = 6.4, 3H), 1.10 (s, 9H);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  144.8, 114.1, 69.2, 66.5, 64.9, 58.8, 57.1, 25.9, 23.9; IR (film): 2971, 2929, 2865, 1361, 1129  $\text{cm}^{-1}$ ; HRMS–APCI ( $m/z$ )  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{11}\text{H}_{20}\text{NO}_2^+$ , 198.14886; found, 198.14936.

The structure of **27** was verified by 2D-NOESY, as the following interaction was observed:

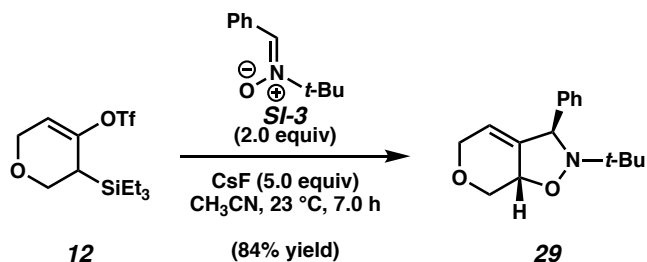
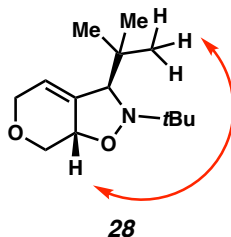






**Isoxazolidine 28.** Following concentration under reduced pressure, the crude residue was obtained (>20:1 dr, average of two experiments). Purification by flash chromatography (9:1 hexanes:EtOAc) afforded isoxazolidine **28** as a white powder in 77% yield (average of two experiments). Isoxazolidine **28**: Mp: 103–105 °C;  $R_f$  0.14 (9:1 hexanes:EtOAc);  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.45 (s, 1H), 4.30–4.28 (m, 1H), 4.23–4.20 (m, 2H), 4.05–4.02 (m, 1H), 3.31 (s, 1H), 3.17 (t,  $J = 9.8$ , 1H), 1.03 (s, 9H), 0.95 (s, 9H);  $^{13}\text{C-NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.7, 117.6, 71.5, 70.9, 66.9, 64.7, 59.9, 34.3, 27.1, 26.9; IR (film): 2955, 2836, 1595, 1417, 1205  $\text{cm}^{-1}$ ; HRMS–APCI ( $m/z$ )  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_{26}\text{NO}_2^+$ , 240.19581; found, 240.19751.

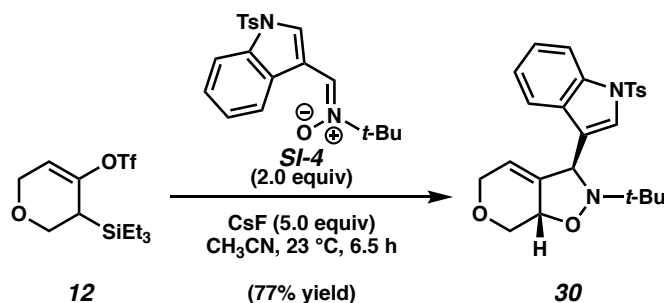
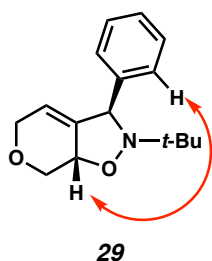
The structure of **28** was verified by 2D-NOESY, as the following interaction was observed:



**Isoxazolidine 29.** Following concentration under reduced pressure, the crude residue was obtained (10.7:1 dr, average of two experiments). Purification by preparative thin layer chromatography (9:1 benzene: $\text{CH}_3\text{CN}$ ) allowed for separation of the two diastereomers, which provided a total yield of 84% (average of two experiments). Major diastereomer **29** was obtained as a white powder. Isoxazolidine **29**: Mp: 111–112 °C;  $R_f$  0.43 (9:1 hexanes:EtOAc);  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.49–7.47 (m, 2H), 7.33–7.30 (m, 2H), 7.25–7.22 (m, 1H), 5.44 (app quint,

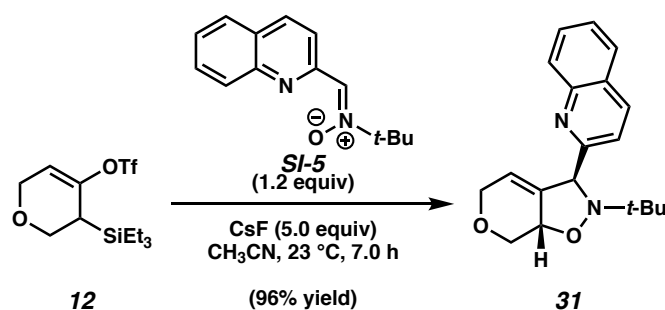
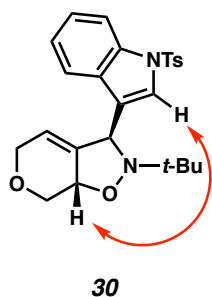
$J = 2.0$ , 1H), 4.62 (s, 1H), 4.50–4.46 (m, 1H), 4.31 (dd,  $J = 9.6$ , 5.6, 1H), 4.13–4.02 (m, 2H), 3.17 (app t,  $J = 9.4$ , 1H), 1.08 (s, 9H);  $^{13}\text{C}$ -NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  144.8, 143.8, 128.6, 127.3, 127.0, 115.5, 70.1, 66.3, 65.7, 65.0, 59.0, 26.2; IR (film): 2972, 2931, 2867, 1492, 1453  $\text{cm}^{-1}$ ; HRMS–APCI ( $m/z$ ) [ $\text{M} + \text{H}$ ] $^+$  calcd for  $\text{C}_{16}\text{H}_{22}\text{NO}_2^+$ , 260.16451; found, 260.16520.

The structure of **29** was verified by 2D-NOESY, as the following interaction was observed:



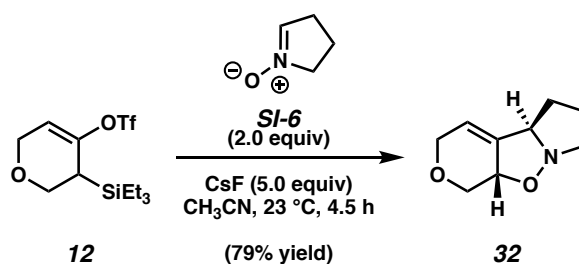
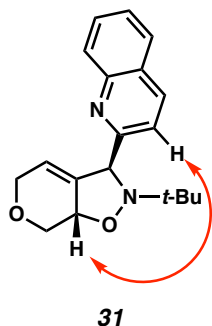
**Isoxazolidine 30.** Following concentration under reduced pressure, the crude residue was obtained (>7.7:1 dr, average of two experiments). Purification by preparative thin layer chromatography (2:2:1 hexanes:benzene:Et<sub>2</sub>O) allowed for separation of the two diastereomers, which provided a total yield of 77% (average of two experiments). Major diastereomer **30** was obtained as a white foam. Isoxazolidine **30**:  $R_f$  0.27 (5:1 hexanes:EtOAc);  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.98 (d,  $J = 8.3$ , 1H), 7.75–7.70 (m, 4H), 7.33–7.29 (m, 1H), 7.25–7.21 (m, 1H), 7.21–7.16 (m, 2H), 5.55–5.52 (m, 1H), 4.87 (s, 1H), 4.51–4.45 (m, 1H), 4.30 (dd,  $J = 10.2$ , 5.6, 1H), 4.06–4.02 (m, 2H), 3.18 (app t,  $J = 9.0$ , 1H), 2.32 (s, 3H), 1.06 (s, 9H);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  144.8, 142.9, 135.8, 135.3, 129.8, 129.0, 126.8, 125.0, 124.8, 124.0, 123.1, 120.3, 115.6, 114.0, 69.8, 66.1, 64.2, 58.8, 58.2, 25.8, 21.5; IR (film): 2971, 2931, 2868, 1445, 1363  $\text{cm}^{-1}$ ; HRMS–APCI ( $m/z$ ) [ $\text{M} + \text{H}$ ] $^+$  calcd for  $\text{C}_{25}\text{H}_{29}\text{N}_2\text{O}_4\text{S}^+$ , 453.18425; found, 453.18223.

The structure of **30** was verified by 2D-NOESY, as the following interaction was observed:



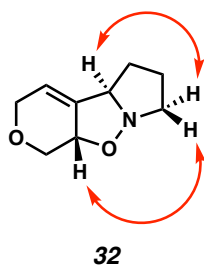
**Isoxazolidine 31.** Following concentration under reduced pressure, the crude residue was obtained (2.8:1 dr, average of two experiments). Purification by preparative thin layer chromatography (2:2:1 hexanes:CH<sub>2</sub>Cl<sub>2</sub>:Et<sub>2</sub>O) allowed for separation of the two diastereomers, which provided a total yield of 96% (average of two experiments). Major diastereomer **31** was obtained as a white powder. Isoxazolidine **31**: *R<sub>f</sub>* 0.33 (5:1 hexanes:EtOAc); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 8.13 (d, *J* = 8.5, 1H), 8.06 (d, *J* = 7.8, 1H), 7.86 (d, *J* = 8.9, 1H), 7.80 (dd, *J* = 8.2, 1.3, 1H), 7.70 (ddd, *J* = 9.0, 7.8, 1.4, 1H), 7.51 (ddd, *J* = 9.0, 7.5, 1.2, 1H), 5.66 (app quint, *J* = 2.0, 1H), 5.02–5.01 (m, 1H), 4.60–4.56 (m, 1H), 4.35 (dd, *J* = 10.0, 5.5, 1H), 4.07 (app q, *J* = 2.6, 2H), 3.21 (dd, *J* = 10.2, 9.0, 1H), 1.10 (s, 9H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ 163.0, 147.6, 143.3, 136.8, 129.6, 129.1, 127.82, 128.76, 126.3, 120.1, 117.2, 70.5, 68.5, 66.3, 65.1, 59.1, 26.0; IR (film): 3061, 2971, 2866, 1597, 1502 cm<sup>-1</sup>; HRMS–APCI (*m/z*) [*M* + *H*]<sup>+</sup> calcd for C<sub>19</sub>H<sub>23</sub>N<sub>2</sub>O<sub>5</sub><sup>+</sup>, 311.17540; found, 311.17394.

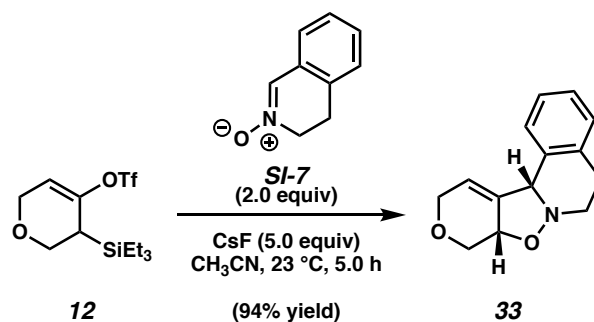
The structure of **31** was verified by 2D-NOESY, as the following interaction was observed:



**Isoxazolidine 32.** Following concentration under reduced pressure, the crude residue was obtained (8.7:1 dr, average of two experiments). Purification by sequential preparative thin layer chromatography (99:1 CHCl<sub>3</sub>:MeOH, eluted once, then 19:1 Et<sub>2</sub>O:EtOAc, eluted twice) allowed for separation of the two diastereomers, which provided a total yield of 79% (average of two experiments). Major diastereomer **32** was obtained as a colorless oil. Isoxazolidine **32**: *R<sub>f</sub>* 0.26 (19:1 Et<sub>2</sub>O:EtOAc); <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): δ 5.62–5.57 (m, 1H), 4.45–4.39 (m, 1H), 4.23–4.15 (m, 3H), 4.09–4.03 (m, 1H), 3.29–3.19 (m, 2H), 3.09 (dd, *J* = 10.0, 9.6, 1H), 2.11–2.03 (m, 1H), 1.91–1.82 (m, 1H), 1.81–1.71 (m, 2H); <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>): δ 143.5, 116.2, 69.1, 66.9, 66.6, 64.7, 58.1, 32.2, 25.3; IR (film): 3032, 1695, 1414, 1229, 1109 cm<sup>-1</sup>; HRMS–APCI (*m/z*) [*M* + H]<sup>+</sup> calcd for C<sub>9</sub>H<sub>14</sub>NO<sub>2</sub><sup>+</sup>, 168.10191; found, 168.10434.

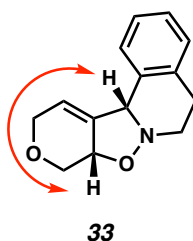
The structure of **32** was verified by 2D-NOESY, as the following interaction was observed:

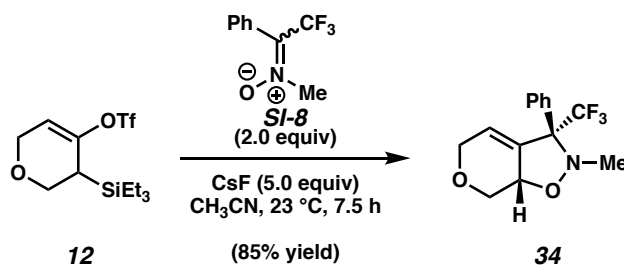




**Isoxazolidine 33.** Following concentration under reduced pressure, the crude residue was obtained (5.3:1 dr, average of two experiments). Purification by preparative thin layer chromatography (4:1 benzene:CH<sub>3</sub>CN) allowed for separation of the two diastereomers, which provided a total yield of 94% (average of two experiments). Major diastereomer **33** was obtained as a colorless oil. Isoxazolidine **33**: *R<sub>f</sub>* 0.53 (1:1 hexanes:EtOAc); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 7.29–7.19 (m, 2H), 7.18–7.13 (m, 2H), 5.34 (app quint, *J* = 2.2, 1H), 5.00 (br s, 1H), 4.54–4.46 (m, 1H), 4.35 (dd, *J* = 10.3, 5.5, 1H), 4.25 (dq, *J* = 16.9, 2.4, 1H), 3.99 (dq, *J* = 16.9, 2.6, 1H), 3.21 (ddd, *J* = 10.1, 4.5, 3.8, 1H), 3.07–2.98 (m, 2H), 2.84 (ddd, *J* = 11.7, 10.5, 3.0, 1H), 2.73 (dt, *J* = 16.2, 3.5, 1H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ 141.0, 134.4, 131.9, 128.6, 128.1, 127.2, 126.3, 119.3, 71.7, 68.9, 64.7, 64.4, 51.3, 28.9; IR (film): 3023, 2964, 2923, 1494, 1454 cm<sup>-1</sup>; HRMS–APCI (*m/z*) [*M* + *H*]<sup>+</sup> calcd for C<sub>14</sub>H<sub>16</sub>NO<sub>2</sub><sup>+</sup>, 230.11756; found, 230.11828.

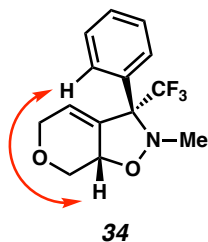
The structure of **33** was verified by 2D-NOESY, as the following interaction was observed:





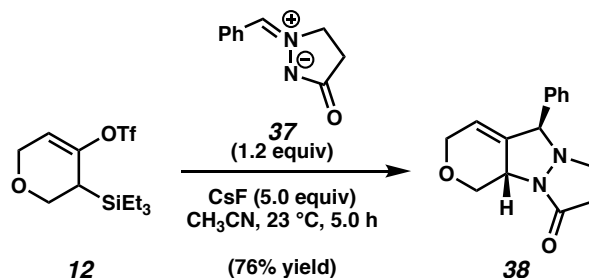
**Isoxazolidine 34.** In this reaction, nitrone **SI-8** was utilized as a mixture of double bond isomers (5:1 ratio, major isomer depicted). Following concentration under reduced pressure, the crude residue was obtained (5.5:1 dr, average of two experiments). Purification by preparative thin layer chromatography (5:1 hexanes:EtOAc) allowed for separation of the two diastereomers, which provided a total yield of 85% (average of two experiments). Major diastereomer **34** was obtained as a white solid. Isoxazolidine **34**: Mp: 67–68 °C;  $R_f$  0.37 (9:1 hexanes:EtOAc);  $^1\text{H}$ -NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.67–7.62 (m, 2H), 7.42–7.38 (m, 3H), 6.03–6.00 (m, 1H), 4.63–4.57 (m, 1H), 4.41 (dt,  $J = 17.3, 2.4$ , 1H), 4.32 (dd,  $J = 9.9, 5.4$ , 1H), 4.20 (dt,  $J = 17.3, 2.9$ , 1H), 3.25 (app t,  $J = 9.4$ , 1H), 2.62 (s, 3H);  $^{13}\text{C}$ -NMR (125 MHz,  $\text{CDCl}_3$ ): 139.3, 133.0, 129.3, 128.74, 128.72, 128.6, 125.2 (q,  $J = 287$ ), 122.8 (q,  $J = 1.6$ ), 70.7, 66.1, 64.9, 41.4; IR (film): 2971, 2875, 1450, 1268, 1157  $\text{cm}^{-1}$ ; HRMS–APCI ( $m/z$ )  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{17}\text{H}_{21}\text{F}_3\text{NO}_2^+$ , 286.10494; found, 286.10572.

The structure of **34** was verified by 2D-NOESY, as the following interaction was observed:



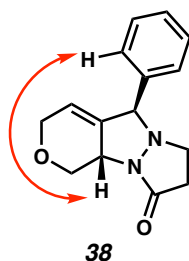
**D. Additional (3+2) and (2+2) Trapping Experiments.**

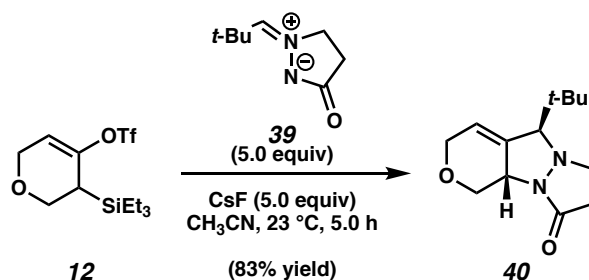
**Representative Procedure (Preparation of pyrazolidine **38** is used as an example).**



**Pyrazolidine **38**.** To a stirred solution of silyl triflate **12** (51.3 mg, 0.148 mmol, 1.0 equiv) and azomethineimine **37** (31.0 mg, 0.178 mmol, 1.2 equiv) in CH<sub>3</sub>CN (1.48 mL) was added CsF (112 mg, 0.740 mmol, 5.0 equiv). The reaction vessel was sealed with a PTFE lined cap and allowed to stir at 23 °C for 5 h. Then, the crude reaction mixture was filtered by passage through a plug of silica gel (EtOAc eluent, 10 mL). Concentration under reduced pressure yielded the crude residue (7.6:1 dr, average of two experiments). Purification by preparative thin layer chromatography (2:1 benzene:CH<sub>3</sub>CN) allowed for separation of the two diastereomers, which were obtained in a total yield of 76% (average of two experiments). The major diastereomer **38** was obtained as a colorless oil. Pyrazolidine **38**: *R<sub>f</sub>* 0.12 (1:1 hexanes:EtOAc); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 7.41–7.31 (m, 5H), 5.61–5.55 (m, 1H), 4.78 (dd, *J* = 10.2, 4.8, 1H), 4.31–4.22 (m, 3H), 4.20–4.11 (m, 1H), 3.54–3.44 (m, 2H), 3.05 (app q, *J* = 9.2, 1H), 2.70–2.55 (m, 2H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ 167.9, 141.3, 138.5, 129.1, 128.5, 128.0, 119.7, 72.0, 65.1, 51.8, 49.7, 49.6, 34.7; IR (film): 3060, 2981, 2927, 1678, 1453 cm<sup>-1</sup>; HRMS–APCI (*m/z*) [*M* + *H*]<sup>+</sup> calcd for C<sub>15</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup>, 257.12845; found, 257.12933.

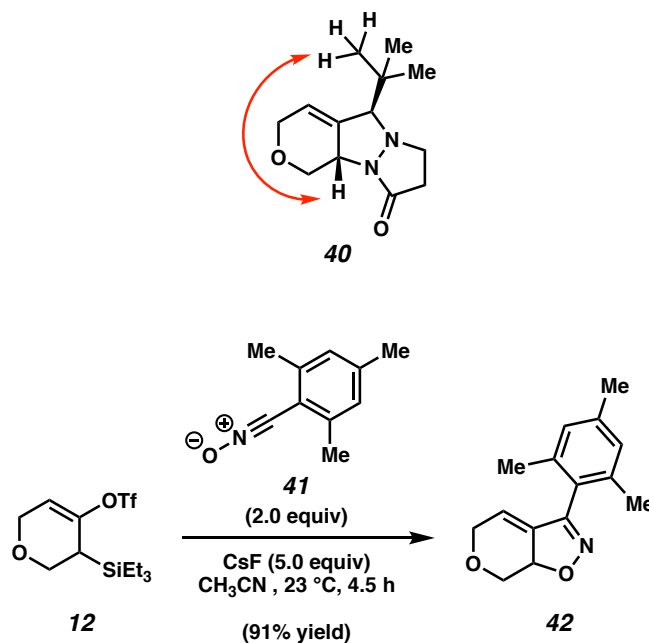
The structure of **38** was verified by 2D-NOESY, as the following interaction was observed:





**Pyrazolidine 40.** Following concentration under reduced pressure, the crude residue was obtained (>20:1 dr, average of two experiments). Purification by preparative thin layer chromatography (2:1 benzene: CH<sub>3</sub>CN) afforded Pyrazolidine **40** as a white powder in 83% yield (average of two experiments). Pyrazolidine **40**: Mp: 120–122 °C; *R<sub>f</sub>* 0.15 (1:1 hexanes:EtOAc); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 5.57 (app quint, *J* = 2.0, 1H), 4.88 (dd, *J* = 10.7, 5.4, 1H), 4.27 (dq, *J* = 16.8, 2.4, 1H), 4.14–4.06 (m, 1H), 3.93–3.85 (m, 1H), 3.67–3.58 (m, 1H), 3.42 (dd, *J* = 10.6, 9.8, 1H), 2.91–2.77 (m, 3H), 2.57–2.45 (m, 1H), 0.93 (s, 9H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ 164.0, 138.0, 120.7, 78.9, 65.7, 65.2, 56.3, 51.1, 35.3, 35.2, 26.3; IR (film): 2955, 2868, 1679, 1445, 1421 cm<sup>−1</sup>; HRMS–APCI (*m/z*) [*M* + *H*]<sup>+</sup> calcd for C<sub>13</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup>, 237.15975; found, 237.16054.

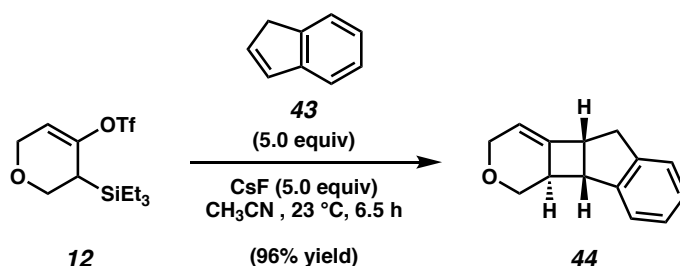
The structure of **40** was verified by 2D-NOESY, as the following interaction was observed:



**Isoxazoline 42.** Purification by preparative thin layer chromatography (5:1 hexanes:EtOAc) afforded isoxazoline **42** as a clear, colorless oil (91% yield, average of two experiments).

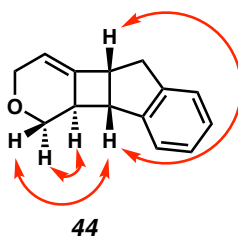


Isoxazoline **42**:  $R_f$  0.36 (9:1 hexanes:EtOAc);  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.94–6.90 (m, 2H), 5.60–5.58 (m, 1H), 5.02–4.96 (m, 1H), 4.55 (dd,  $J = 9.6, 5.4$ , 1H), 4.36 (ddd,  $J = 18.4, 4.6, 2.4$ , 1H), 4.20 (ddd,  $J = 18.4, 5.0, 3.0$ , 1H), 3.35 (app t,  $J = 9.3$ , 1H), 2.31 (s, 3H), 2.20 (s, 3H), 2.18 (s, 3H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.7, 140.6, 139.2, 137.6, 137.3, 128.51, 128.48, 123.6, 120.1, 75.0, 66.0, 64.5, 21.2, 20.0, 19.7; IR (film) 2975, 2865, 1736, 1612, 1113  $\text{cm}^{-1}$ ; HRMS–APCI ( $m/z$ )  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{15}\text{H}_{17}\text{NO}_2^+$ , 244.13321; found, 244.13475.



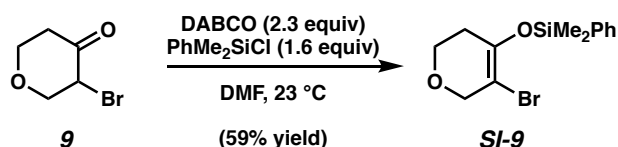
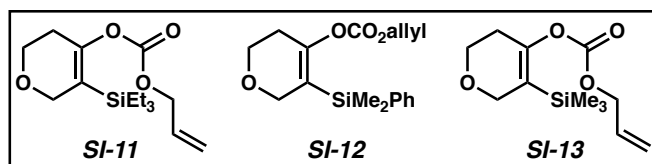
**Cyclobutane 44.** Following concentration under reduced pressure, the crude residue was obtained (5.2:1 dr, average of two experiments). Purification by successive preparative thin layer chromatography (20:5:1 hexanes: $\text{CH}_2\text{Cl}_2$ : $\text{Et}_2\text{O}$ , eluted twice) allowed for separation of the two diastereomers, which provided a total yield of 96% (average of two experiments). Major diastereomer **44** was obtained as a colorless oil. Cyclobutane **44**:  $R_f$  0.48 (9:1 hexanes:EtOAc);  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.30–7.23 (m, 1H), 7.21–7.12 (m, 3H), 5.47–5.42 (m, 1H), 4.32–4.26 (m, 1H), 4.19–4.10 (m, 2H), 3.83–3.75 (m, 1H), 3.63–3.59 (m, 1H), 3.34–3.25 (m, 2H), 3.21 (app t,  $J = 9.8$ , 1H), 3.07–3.00 (m, 1H);  $^{13}\text{C-NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.0, 145.9, 141.4, 126.8, 126.7, 125.3, 123.5, 113.0, 66.9, 65.5, 50.1, 49.3, 48.8, 37.3; IR (film): 3067, 3041, 2939, 2844, 1480  $\text{cm}^{-1}$ ; HRMS–APCI ( $m/z$ )  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_{15}\text{O}^+$ , 199.11174; found, 199.11236.

The structure of **44** was verified by 2D-NOESY, as the following interaction was observed:

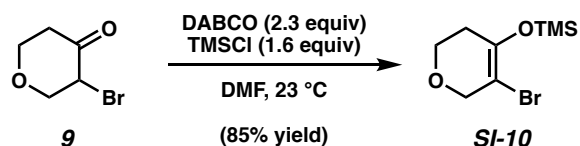


**E. Synthesis of the Allylation Substrates.**

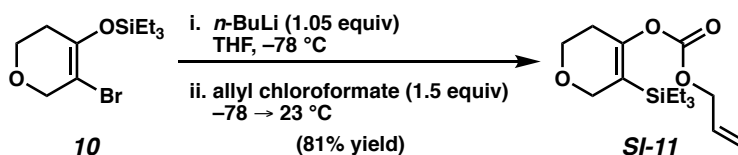
In addition to **45**, enol carbonates **SI-11**, **SI-12**, and **SI-13** were prepared in order to determine the optimal substrate and conditions for the asymmetric allylic alkylation. The enol carbonates were then tested in the subsequent Pd-catalyzed allylic alkylation in Section F.



**Silyl enol ether SI-9.** To a stirred solution of known bromo ketone **9**<sup>10</sup> (300 mg, 1.68 mmol, 1.0 equiv) in DMF (1.52 mL) and PhMe<sub>2</sub>SiCl (0.45 mL, 2.68 mmol, 1.6 equiv) was added DABCO (432 mg, 3.85 mmol, 2.3 equiv). The reaction vessel was then purged with N<sub>2</sub> and sealed with a PTFE lined cap, before allowing it to stir at 23 °C. After 12 h, the mixture was cooled to –40 °C for 10 min before quenching the reaction with sat. NaHCO<sub>3</sub> (2.0 mL) and water (4.0 mL). The layers were then separated and the aqueous layer was then extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with water (2 x 10 mL) and brine (1 x 10 mL), before being dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The resultant crude oil was purified via flash chromatography (19:1 hexanes:EtOAc) to afford silyl enol ether **SI-9** as a colorless oil (308.5 mg, 59% yield). Silyl enol ether **SI-9**: *R<sub>f</sub>* 0.48 (9:1 hexanes:EtOAc); <sup>1</sup>H-NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.59–7.53 (m, 2H), 7.20–7.14 (m, 3H), 4.10–4.07 (m, 2H), 3.27 (t, *J* = 5.5, 2H), 1.83–1.77 (m, 2H), 0.37 (s, 6H); <sup>13</sup>C-NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>): δ 145.1, 137.5, 133.7, 130.3, 98.8, 69.8, 64.7, 32.9, –0.5; IR (film): 3071, 2964, 2828, 1675, 1428 cm<sup>–1</sup>; HRMS–APCI (*m/z*) [*M* + H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>18</sub>BrO<sub>2</sub>Si<sup>+</sup>, 313.02540; found, 313.02630.

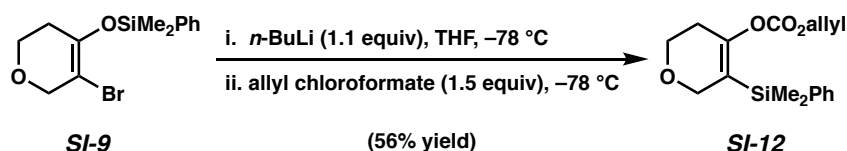


**Silyl enol ether SI-10.** To a stirred solution of known bromo ketone **9**<sup>10</sup> (100 mg, 0.559 mmol, 1.0 equiv) and TMSCl (0.11 mL, 0.894 mmol, 1.6 equiv) in DMF (0.51 mL) was added DABCO (144 mg, 1.28 mmol, 2.3 equiv). The reaction vessel was then purged with N<sub>2</sub> and sealed with a PTFE lined cap, before allowing it to stir at 23 °C. After 22 h, the mixture was cooled to –40 °C for 10 min and quenched with sat. aq. NaHCO<sub>3</sub> (0.5 mL) and deionized water (0.5 mL). The layers were then separated and the aqueous layer was extracted with EtOAc (3 x 3 mL). The combined organic layers were washed with water (2 x 5 mL) and brine (1 x 5 mL), before being dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The resultant crude oil was purified via flash chromatography (19:1 hexanes:EtOAc) to afford silyl enol ether **SI-10** as a colorless oil (119.1 mg, 85% yield). Silyl enol ether **SI-10**: *R<sub>f</sub>* 0.49 (9:1 hexanes:EtOAc); <sup>1</sup>H-NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 4.10 (t, *J* = 2.3, 2H), 3.35 (t, *J* = 5.5, 2H), 1.86–1.81 (m, 2H), 0.10 (s, 9H); <sup>13</sup>C-NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ 144.7, 98.2, 69.4, 64.4, 32.6, 0.4; IR (film): 2968, 2861, 1675, 1265, 1252 cm<sup>–1</sup>; HRMS–APCI (*m/z*) [*M* + *H*]<sup>+</sup> calcd for C<sub>8</sub>H<sub>15</sub>BrO<sub>2</sub>Si<sup>+</sup>, 253.00770; found, 253.00876.

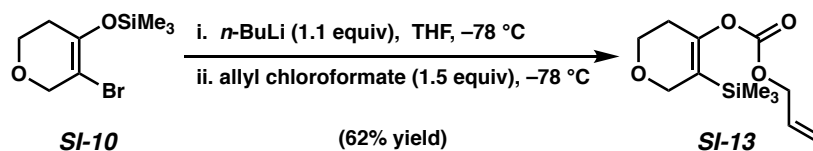


**Enol carbonate SI-11.** To a solution of known silyl enol ether **10**<sup>10</sup> (330 mg, 1.13 mmol, 1.00 equiv) in THF (13.2 mL) at –78 °C was added *n*-BuLi (2.24 M in hexanes, 0.527 mL, 1.18 mmol, 1.05 equiv) dropwise over 2.0 min. The solution was stirred for 34 min at –78 °C, before neat allyl chloroformate (0.180 mL, 1.69 mmol, 1.5 equiv) was then added dropwise over 1 min and the reaction was allowed to stir for 1.0 h at –78 °C, before warming to 23 °C. After stirring for 2.0 h, the reaction was quenched with water (10 mL). The layers were then separated and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were then dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The resulting crude oil was purified by flash chromatography (19:1 hexanes:EtOAc) to afford enol carbonate **SI-11** (273.1 mg, 81% yield) as a colorless oil. Enol carbonate **SI-11**: *R<sub>f</sub>* 0.58 (5:1 hexanes:EtOAc);

$^1\text{H}$ -NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.99–5.91 (m, 1H), 5.39 (dq,  $J = 17.2, 1.4$ , 1H), 5.30 (dq,  $J = 1.4, 1.3$ , 1H), 4.66 (dt,  $J = 5.9, 1.3$ , 2H), 4.22 (t,  $J = 2.6$ , 2H), 3.85 (t,  $J = 5.6$ , 6H), 2.41 (s,  $J = 2.6$ , 2H), 0.93 (t,  $J = 8.0$ , 9H), 0.62 (q,  $J = 8.0$ , 6H);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  152.9, 151.7, 131.5, 120.1, 119.4, 68.8, 67.5, 64.3, 28.1, 7.4, 3.0; IR (film): 2954, 1754, 1657, 1228, 1161  $\text{cm}^{-1}$ ; HRMS–APCI ( $m/z$ ) [ $M + H$ ] $^+$  calcd for  $\text{C}_{15}\text{H}_{27}\text{O}_4\text{Si}^+$ , 299.16731; found, 299.16694.

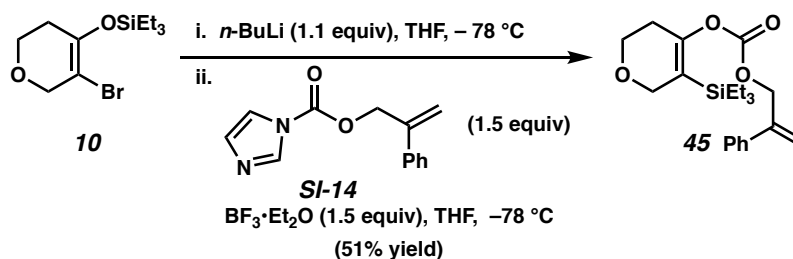


**Enol carbonate SI-12.** To a solution of silyl enol ether **SI-9** (150.0 mg, 0.479 mmol, 1.00 equiv) in THF (5.6 mL) at  $-78\text{ }^\circ\text{C}$  was added  $n\text{-BuLi}$  (2.22 M in hexanes, 0.237 mL, 0.527 mmol, 1.1 equiv) dropwise over 1.0 min. The solution was stirred for 20 min at  $-78\text{ }^\circ\text{C}$ , then neat allyl chloroformate (76.6  $\mu\text{L}$ , 0.718 mmol, 1.5 equiv) was added dropwise over 1 min and the reaction was allowed to stir at  $-78\text{ }^\circ\text{C}$ . After stirring for 4.0 h, the reaction was quenched with water (4.0 mL) at  $-78\text{ }^\circ\text{C}$ . The layers were then separated and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The resulting crude oil was purified by flash chromatography (15:1 hexanes:EtOAc) to afford enol carbonate **SI-12** (84.6 mg, 56% yield) as a colorless oil. Enol carbonate **SI-12**:  $R_f$  0.31 (9:1 hexanes:EtOAc);  $^1\text{H}$ -NMR (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.54–7.49 (m, 2H), 7.39–7.31 (m, 3H), 5.92–5.82 (m, 1H), 5.33–5.27 (m, 1H), 5.25–5.21 (m, 1H), 4.47–4.43 (m, 2H), 4.17–4.14 (m, 2H), 3.78–3.75 (m, 2H), 2.32–2.27 (m, 2H), 1.92 (app quint,  $J = 2.4$ , 2H), 0.34 (s, 6H);  $^{13}\text{C}$ -NMR (125 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  153.4, 153.3, 138.2, 134.7, 132.8, 130.3, 128.8, 121.8, 119.3, 69.4, 67.6, 64.8, 28.7,  $-2.8$ ; IR (film): 2958, 2855, 1755, 1428, 1253  $\text{cm}^{-1}$ ; HRMS–APCI ( $m/z$ ) [ $M + H$ ] $^+$  calcd for  $\text{C}_{17}\text{H}_{23}\text{O}_4\text{Si}^+$ , 319.13601; found, 319.13757.



**Enol carbonate SI-13.** To a solution of silyl enol ether **SI-10** (60.0 mg, 0.239 mmol, 1.00 equiv) in THF (2.8 mL) at  $-78\text{ }^\circ\text{C}$  was added  $n\text{-BuLi}$  (2.25 M in hexanes, 0.117 mL, 0.263 mmol, 1.1 equiv) dropwise over 2.0 min. The solution was stirred for 21 min at  $-78\text{ }^\circ\text{C}$ , then neat allyl

chloroformate (38.2  $\mu$ L, 0.385 mmol, 1.5 equiv) was added dropwise over 1 min and the reaction was allowed to stir at  $-78$  °C. After stirring for 3.0 h, the reaction was quenched with water (2.0 mL). The layers were then separated and the aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layers were then dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The resulting crude oil was purified by flash chromatography (15:1 hexanes:EtOAc) to afford enol carbonate **SI-13** (37.7 mg, 62% yield) as a colorless oil. Enol carbonate **SI-13**:  $R_f$  0.29 (9:1 hexanes:EtOAc);  $^1\text{H}$ -NMR (500 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  5.68–5.59 (m, 1H), 5.07 (dq,  $J$  = 17.2, 1.7, 1H), 4.91 (dq,  $J$  = 10.3, 1.2, 1H), 4.36 (dt,  $J$  = 5.8, 1.4, 2H), 4.13 (t,  $J$  = 2.6, 2H), 3.55 (t,  $J$  = 5.6, 2H), 2.26–2.21 (m, 2H), 0.06 (s, 9H);  $^{13}\text{C}$ -NMR (125 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  153.3, 152.1, 131.9, 122.4, 118.7, 68.5, 67.0, 64.2, 28.3,  $-1.5$ ; IR (film): 2956, 2856, 1755, 1252, 1231  $\text{cm}^{-1}$ ; HRMS–APCI ( $m/z$ ) [ $\text{M} + \text{H}$ ] $^+$  calcd for  $\text{C}_{12}\text{H}_{20}\text{O}_4\text{Si}^+$ , 257.12036; found, 257.12173.



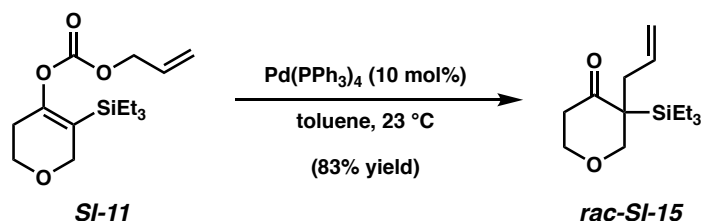
**Enol carbonate 45.** To a solution of silyl enol ether **10** (601.0 mg, 2.05 mmol, 1.00 equiv) in THF (24.1 mL) at  $-78$  °C was added  $n$ -BuLi (2.19 M in hexanes, 1.03 mL, 2.25 mmol, 1.1 equiv) dropwise over 1.0 min. The solution was stirred for 45 min at  $-78$  °C, then a solution of the known imidazole carboxylate<sup>8</sup> **SI-14** (702 mg, 3.07 mmol, 1.50 equiv) and  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (390  $\mu$ L, 2.25 mmol, 1.5 equiv) in THF (4.0 mL) that was prestirred for 35 min (at  $23$  °C) was added dropwise over 5 min and the reaction was allowed to stir at  $-78$  °C. After stirring for 3.0 h the reaction was quenched with water (10.0 mL) at  $-78$  °C. The layers were separated and the aqueous layer was extracted with EtOAc (3 x 50 mL). The combined organic layers were then dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The resulting crude oil was purified by flash chromatography (19:1 hexanes:EtOAc) to afford enol carbonate **45** (391 mg, 51% yield) as a colorless oil. Enol carbonate **45**:  $R_f$  0.54 (9:1 hexanes:EtOAc);  $^1\text{H}$ -NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.47–7.43 (m, 2H), 7.38–7.29 (m, 3H), 5.60 (br s, 1H), 5.44 (q,  $J$  = 1.0, 1H), 5.10 (d,  $J$  = 0.9, 2H), 4.20 (t,  $J$  = 2.6, 2H), 3.82 (t,  $J$  = 5.5, 2H), 2.39–2.34 (m, 2H), 0.89 (t,  $J$  = 7.8, 9H), 0.57 (q,  $J$  = 7.6, 6H);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  152.9, 151.6, 142.1, 137.8,

128.7, 128.3, 126.2, 120.1, 116.4, 69.6, 67.5, 64.3, 28.1, 7.4, 3.0; IR (film): 2953, 1755, 1656, 1230, 1165  $\text{cm}^{-1}$ ; HRMS–APCI ( $m/z$ )  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{31}\text{O}_4\text{Si}^+$ , 375.19861; found, 357.20141.

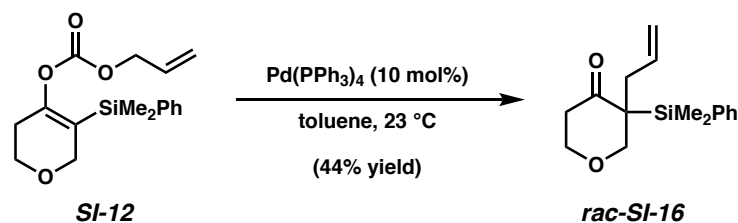
## F. Pd-Catalyzed Decarboxylative Allylic Alkylation

### i. Racemic Reactions Toward $\alpha$ -Silyl Substituted Ketones

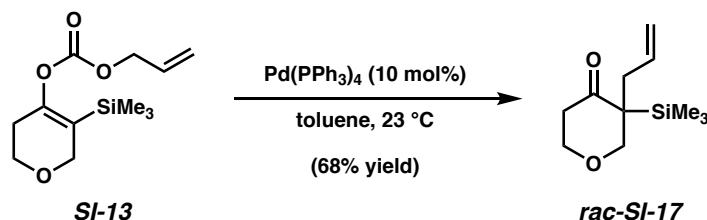
**Representative Procedure for Racemic Reactions (Preparation of silyl ketone SI-15 used as an example)**



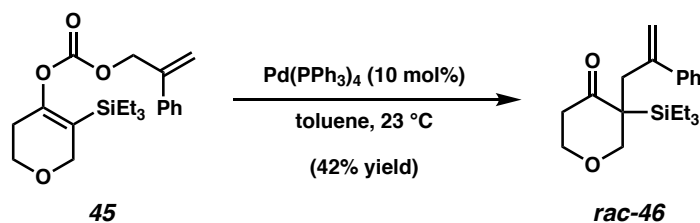
**Silyl Ketone rac-SI-15.** In a nitrogen-filled glovebox, an oven-dried 1-dram vial was equipped with a stir bar, enol carbonate **SI-11** (100 mg, 0.335 mmol, 1.0 equiv), and toluene (1.7 mL). Then  $\text{Pd(PPh}_3)_4$  (38.7 mg, 0.034 mmol, 10 mol%) was added slowly in one portion, before sealing the vial with a PTFE-lined cap. The reaction was then allowed to stir for 20 h at 23 °C before the addition of hexanes (2 mL). After stirring for 2 min, the crude reaction mixture was filtered by passage through a plug of silica gel ( $\text{Et}_2\text{O}$  eluent), and concentrated under reduced pressure. The resulting crude oil was purified via flash chromatography (19:1 hexanes:EtOAc), to provide silyl ketone **rac-SI-15** as a colorless oil (70.5 mg, 83% yield). Silyl ketone **rac-SI-15**:  $R_f$  0.58 (5:1 hexanes:EtOAc);  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.77–5.67 (m, 1H), 5.05–4.96 (m, 2H), 4.19–4.13 (m, 1H), 4.10 (dd,  $J = 11.8, 1.3$ , 1H), 3.76 (d,  $J = 11.7$ , 1H), 3.69 (ddd,  $J = 11.4, 11.4, 4.0$ , 1H), 2.99–2.93 (m, 1H), 2.55 (ddd,  $J = 16.6, 11.5, 7.7$ , 1H), 3.32 (ddd,  $J = 16.6, 4.0, 2.0$ , 1H), 1.92 (dd,  $J = 14.1, 8.8$ , 1H), 1.00 (t,  $J = 7.9$ , 9H), 0.80–0.66 (m, 6H);  $^{13}\text{C-NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  208.7, 135.3, 117.6, 71.2, 67.0, 50.5, 41.3, 35.1, 7.8, 2.9; IR (film): 2956, 1682, 1211, 1187, 1005  $\text{cm}^{-1}$ ; HRMS–APCI ( $m/z$ )  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_{26}\text{O}_2\text{Si}^+$ , 255.17748; found, 255.17914.



**Silyl ketone rac-SI-16.** Purification by preparative thin layer chromatography (9:1 hexanes:EtOAc) afforded silyl ketone **rac-SI-16** as a colorless oil (44% yield). Silyl ketone **rac-SI-16**:  $R_f$  0.14 (3:1 hexanes:EtOAc);  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.55–7.51 (m, 2H), 7.43–7.35 (m, 3H), 5.69–5.59 (m, 1H), 5.00–4.90 (m, 2H), 4.07 (dd,  $J = 11.8, 1.4$ , 1H), 4.05–4.00 (m, 1H), 3.70 (d,  $J = 11.7$ , 1H), 3.68–3.62 (m, 1H), 2.88 (ddt,  $J = 14.2, 5.5, 1.6$ , 1H), 2.22–2.18 (m, 2H), 1.88 (dd,  $J = 14.3, 8.7$ , 1H), 0.49 (s, 3H), 0.42 (s, 3H);  $^{13}\text{C-NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  208.5, 135.1, 134.8, 134.7, 129.8, 127.9, 117.6, 71.2, 67.0, 50.4, 40.7, 34.7, –3.6, –4.8; IR (film): 3071, 2963, 2853, 1681, 1428  $\text{cm}^{-1}$ ; HRMS–APCI ( $m/z$ )  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{16}\text{H}_{23}\text{O}_2\text{Si}^+$ , 275.14618; found, 275.14746.



**Silyl ketone rac-SI-17.** Purification by flash chromatography (15:1 hexanes:EtOAc) afforded silyl ketone **rac-SI-17** as a colorless oil (68% yield). Silyl ketone **rac-SI-17**:  $R_f$  0.26 (9:1 hexanes:EtOAc);  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.77–5.67 (m, 1H), 5.05–4.96 (m, 2H), 4.19–4.13 (m, 1H), 4.07 (d,  $J = 11.8$ , 1H), 3.78 (d,  $J = 11.8$ , 1H), 3.70 (ddd,  $J = 11.6, 11.6, 3.9$ , 1H), 2.85 (dd,  $J = 14.2, 5.4$ , 1H), 2.54–2.45 (m, 1H), 2.36–2.29 (m, 1H), 1.89 (dd,  $J = 14.3, 8.8$ , 1H), 0.13 (s, 9H);  $^{13}\text{C-NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  208.5, 135.0, 117.7, 71.1, 67.1, 50.1, 41.2, 34.5, –2.5; IR (film): 3076, 2925, 2853, 1682, 1251  $\text{cm}^{-1}$ ; HRMS–APCI ( $m/z$ )  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{11}\text{H}_{21}\text{O}_2\text{Si}^+$ , 213.13053; found, 213.13138.



**Silyl ketone rac-46.** Purification by preparative thin layer chromatography (9:1 hexanes:EtOAc) afforded silyl ketone **rac-46** as a colorless oil (42% yield). Silyl ketone **rac-46**:  $R_f$  0.34 (9:1 hexanes:EtOAc);  $^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.32–7.27 (m, 4H), 7.26–7.22 (m, 1H), 5.20 (d,  $J = 1.4$ , 1H), 5.07 (s, 1H), 3.98–3.92 (m, 2H), 3.74–3.69 (m, 2H), 3.41 (ddd,  $J = 11.1$ , 11.1, 4.9, 1H), 2.44 (d,  $J = 14.4$ , 1H), 2.36 (ddd,  $J = 17.6$ , 10.7, 8.2, 1H), 1.94 (ddd,  $J = 17.7$ , 4.8, 2.5, 1H), 1.02 (t,  $J = 7.9$ , 9H), 0.84–0.69 (m, 6H);  $^{13}\text{C-NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  208.3, 147.0, 141.7, 128.1, 127.5, 127.4, 116.8, 70.3, 66.1, 50.7, 40.1, 35.7, 7.8, 2.8; IR (film): 2955, 2877, 1680, 1444, 1188  $\text{cm}^{-1}$ ; HRMS–APCI ( $m/z$ ) [ $M + H$ ] $^+$  calcd for  $\text{C}_{21}\text{H}_{31}\text{O}_4\text{Si}^+$ , 331.20878; found, 331.20983.

## ii. Additional Asymmetric Allylic Alkylation Optimization Reactions.

### Representative Procedure for Optimization Reactions for Table 3, Table S1, Table S2, and Table S3.

In a nitrogen-filled glovebox, an oven-dried 1-dram vial was equipped with a stir bar, ligand (6.25  $\mu\text{mol}$ , 12.5 mol %),  $\text{Pd}_2(\text{dba})_3$  (2.50  $\mu\text{mol}$ , 5 mol %), and toluene (0.75 mL). The vial was then capped with a PTFE-lined cap and stirred at 23 °C for 30 min before cooling to the desired temperature. A solution of enol carbonate starting material (0.05 mmol, 1 equiv) in toluene (0.75 mL) was slowly added over 1 min to the catalyst mixture. The vial was sealed with a PTFE-lined cap and stirred at the desired temperature for 20 h. The crude reaction mixture was filtered through a silica plug, eluted with  $\text{Et}_2\text{O}$ , and concentrated under reduced pressure. 1,3,5-Trimethoxybenzene was used then added and used as an external standard in quantitative NMR analysis.



Table S1. Additional Optimization Experiments.

entry	ligand	solvent	temp (°C)	% conversion <sup>b</sup>	% ee <sup>c</sup>
1	L1	toluene	23	>95	21
2	L2	toluene	23	>95	2
3	L3	toluene	23	>95	7
4	L4	toluene	23	>95	13
5	L5	toluene	23	>95	0
6	47	toluene	23	>95	62
7	L7	toluene	23	>95	53
8	L8	toluene	23	47	61
9	L9	toluene	23	>95	58
10	47	THF	23	>95	47
11	47	1,4-dioxane	23	>95	57
12	47	MTBE	23	>95	52
13	47	benzene	23	>95	60
14	47	2:1 hexanes:toluene	23	>95	61
15	47	toluene	0	>95	68
16	47	toluene	−10	>95	70

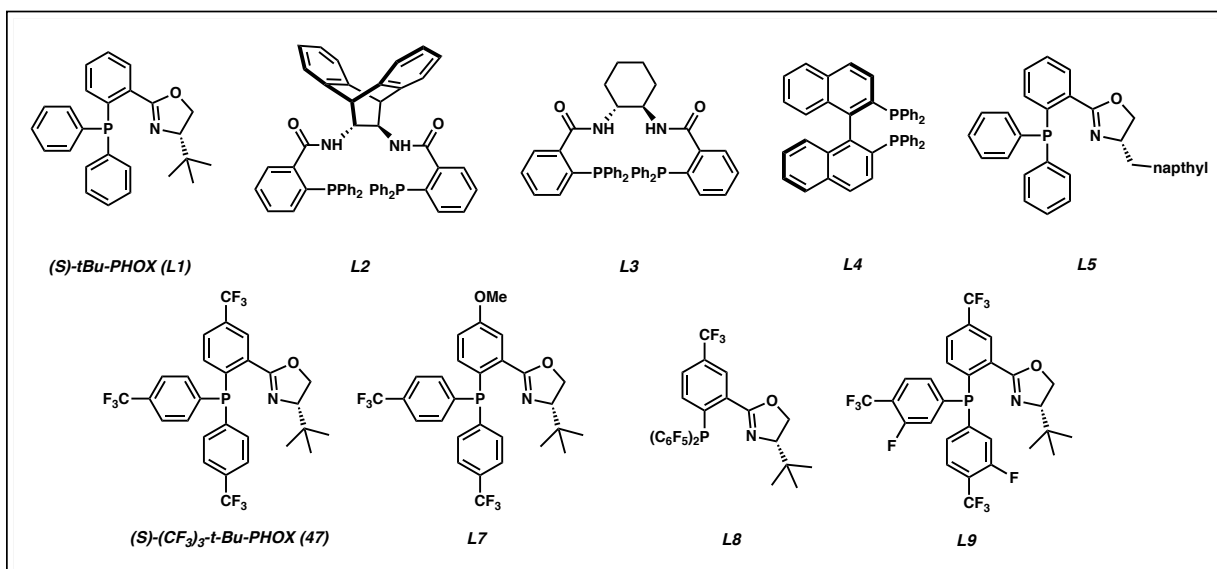
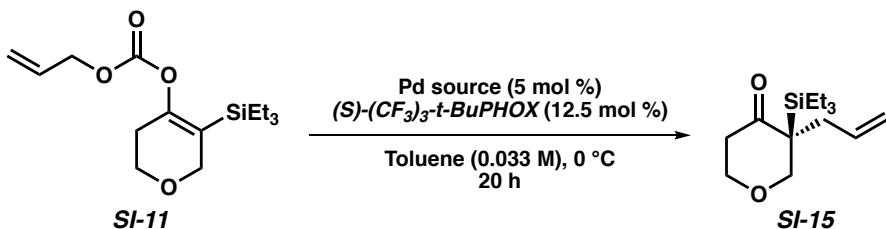
<sup>a</sup>Conditions: enol carbonate (0.05 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (5 mol %), and ligand (12.5 mol %) for 20 h.<sup>b</sup>Conversion determined by <sup>1</sup>H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as a standard.<sup>c</sup>Determined by chiral SFC analysis of the isolated product.

Table S2. Testing Alternative Palladium Sources.

			
entry	Pd source	% conversion <sup>b</sup>	% ee <sup>c</sup>
1	Pd <sub>2</sub> (dba) <sub>3</sub>	>95	68
2	Pd(dmdba) <sub>2</sub> <sup>d</sup>	>95	68
3	Pd <sub>2</sub> (pmdba) <sub>3</sub>	>95	68
4	[PdCl(allyl)] <sub>2</sub>	<10	–

<sup>a</sup>Conditions: enol carbonate(0.05 mmol), Pd source (5 mol %), and ligand (12.5 mol %) for 20 h.<sup>b</sup>Conversion determined by <sup>1</sup>H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an external standard.<sup>c</sup>Determined by chiral SFC analysis of isolated product.<sup>d</sup>Used 10 mol% of Pd source.

Table S3. Substrate, Temperature, and Concentration Optimization Experiments.

$\text{Pd}_2(\text{dba})_3$  (5 mol%) or  $\text{Pd}(\text{dmdba})_2$  (10 mol%)<sup>a</sup>  
 ligand (12.5 mol%)  
 toluene (conc.), temperature

**SI-18**  **SI-19**

Entry	Ligand	SiR <sub>3</sub>	R'	temperature	conc. (M)	%ee <sup>b</sup>	yield <sup>c</sup>
1	L1	SiEt <sub>3</sub>	H	23 °C	0.033	25	51%
2	47	SiEt <sub>3</sub>	H	23 °C	0.033	62	85%
3	47	SiMe <sub>2</sub> Ph	H	23 °C	0.033	58	69%
4	47	SiMe <sub>3</sub>	H	23 °C	0.033	70	88%
5	47	SiMe <sub>3</sub>	H	−10 °C	0.005	75	85%
6	47	SiEt <sub>3</sub>	H	−10 °C	0.005	74	95%
7	47	SiEt <sub>3</sub>	Ph	−10 °C	0.005	81	75%

**(S)-tBu-PHOX (L1)**

**(S)-(CF<sub>3</sub>)<sub>3</sub>-tBu-PHOX (47)**

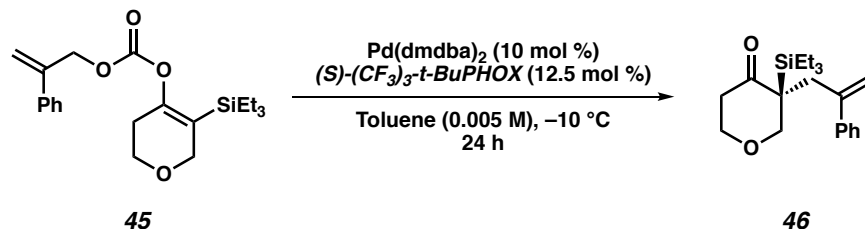
<sup>a</sup>Reactions performed at 23 °C utilized  $\text{Pd}_2(\text{dba})_3$ , while reactions performed at −10 °C utilized  $\text{Pd}(\text{dmdba})_2$ . Utilizing different palladium sources did not have an observable effect on enantioselectivity (see Table S2 for details) and was only utilized to aid purification.

<sup>b</sup>Enantiomeric excesses (ee's) were determined by SFC analysis using a chiral stationary phase (see SI for details).

<sup>c</sup>Yields were determined by <sup>1</sup>H NMR analysis using 1,3,5-trimethoxybenzene as an external standard.

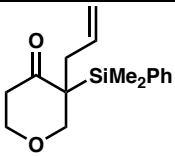
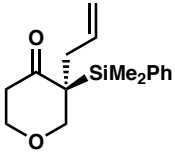
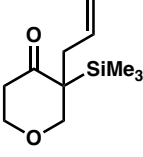
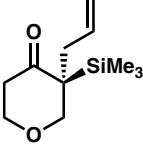
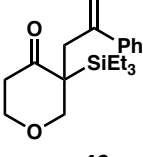
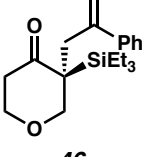
## iii. Optimized Decarboxylative Allylic Alkylation Reactions.

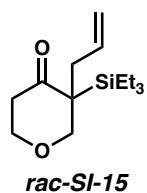
## Representative Procedure for Pd-Catalyzed Decarboxylative Allylic Alkylation Reactions



In a nitrogen-filled glovebox, an oven-dried scintillation vial was equipped with a stir bar, (*S*)-(CF<sub>3</sub>)<sub>3</sub>-*t*-BuPHOX ligand (3.70 mg, 6.25 μmol, 12.5 mol %), Pd(dmdba)<sub>2</sub> (4.08 mg, 5.00 μmol, 10 mol %), and toluene (0.75 mL). The vial was then sealed with a PTFE-lined cap and stirred at 23 °C. After 30 min, the catalyst mixture was diluted with 8.5 mL of toluene and cooled to  $-10\text{ }^\circ\text{C}$ . A solution of enol carbonate starting material (0.05 mmol, 1 equiv) in toluene (0.75 mL) was added dropwise to the catalyst mixture. The vial was sealed with a PTFE-lined septum cap and stirred at  $-10\text{ }^\circ\text{C}$  for 24 h. The crude reaction mixture was filtered through a silica plug (Et<sub>2</sub>O eluent), concentrated under reduced pressure, and purified by flash chromatography to furnish the product. **Silyl ketones SI-15, SI-16, SI-17, and 46** spectral data matched those previously reported (same as pages S24–S26).

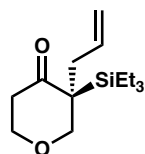
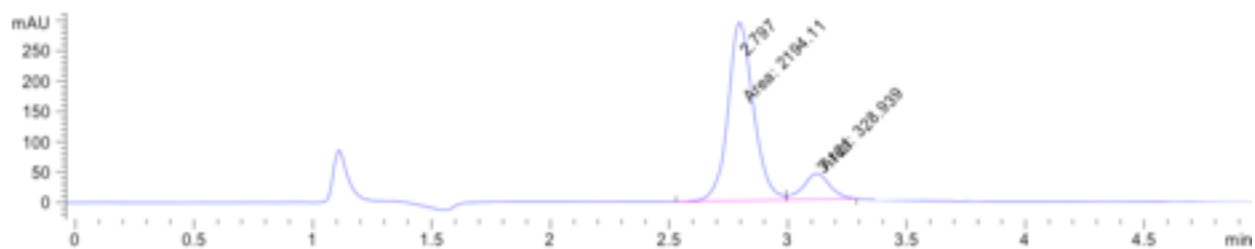
Compound	Method Column/Temp.	Solvent	Method Flow Rate	Retention Times (min)	Enantiomeric Ratio (er)
 <b>rac-SI-15</b>	ChiralPak AD-3/40°C	3% isopropanol in CO <sub>2</sub>	2.5 mL/min	2.81/3.13	49.1:50.9
 <b>SI-15</b>	ChiralPak AD-3/40°C	3% isopropanol in CO <sub>2</sub>	2.5 mL/min	2.80/3.12	87.0:13.0

 <b>rac-SI-16</b>	ChiralPak IC-3/35°C	2% isopropanol in CO <sub>2</sub>	3.5 mL/min	7.47/9.01	50.4/49.6
 <b>SI-16</b>	ChiralPak IC-3/35°C	2% isopropanol in CO <sub>2</sub>	3.5 mL/min	9.76/11.9	77.0/23.0
 <b>rac-SI-17</b>	ChiralPak IC-3/40°C	1% isopropanol in CO <sub>2</sub>	2.5 mL/min	7.05/7.91	49.2/50.8
 <b>SI-17</b>	ChiralPak IC-3/40°C	1% isopropanol in CO <sub>2</sub>	2.5 mL/min	6.67/7.67	87.7/12.3
 <b>rac-46</b>	Chiralcel IC-3/40°C	2% isopropanol in CO <sub>2</sub>	2.5 mL/min	4.37/4.93	50.8/49.2
 <b>46</b>	Chiralcel IC-3/40°C	2% isopropanol in CO <sub>2</sub>	2.5 mL/min	4.47/5.05	90.3/9.7



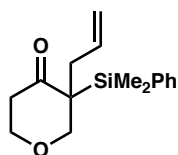
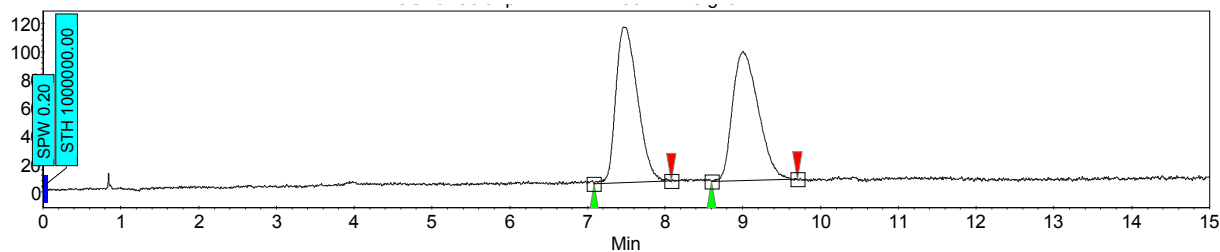
Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.808	MF	0.1586	169.78801	17.84176	49.1226
2	3.132	FM	0.1629	175.85304	17.98790	50.8774

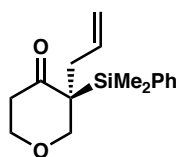
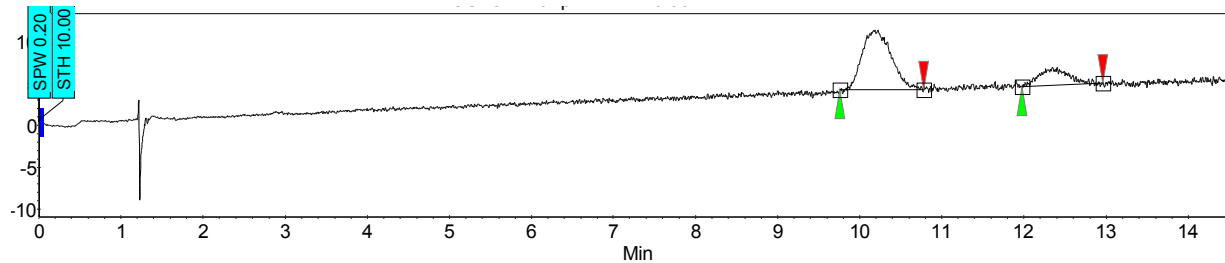
**SI-15**

Signal 1: DAD1 A, Sig=210,8 Ref=360,100

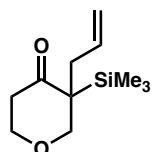
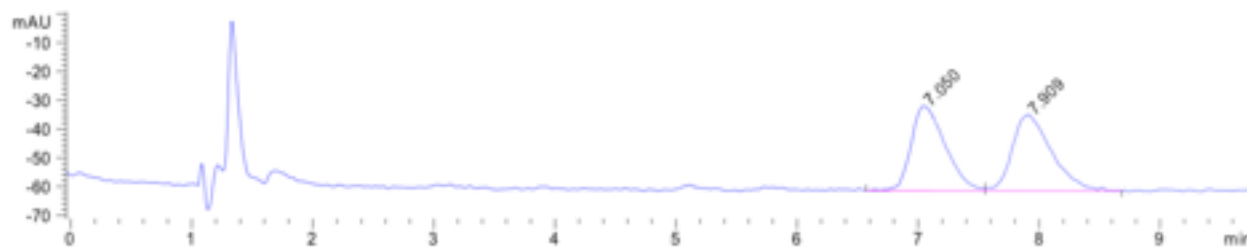
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.797	MF	0.1241	2194.10840	294.65942	86.9626
2	3.121	FM	0.1286	328.93912	42.63451	13.0374

**rac-SI-16**

Index	Name	Start [Min]	Time [Min]	End [Min]	RT Offset [Min]	Quantity [% Area]	Height [μV]	Area [μV.Min]	Area [%]
1	UNKNOWN	7.09	7.47	8.09	0.00	50.38	110.9	35.9	50.385
2	UNKNOWN	8.60	9.01	9.71	0.00	49.62	92.2	35.4	49.615
Total						100.00	203.1	71.3	100.000

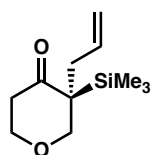
**SI-16**

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μV]	[μV.Min]	[%]
2	UNKNOWN	9.76	10.17	10.78	0.00	77.01	7.1	2.9	77.005
1	UNKNOWN	11.97	12.34	12.96	0.00	22.99	2.2	0.9	22.995
Total						100.00	9.3	3.8	100.000

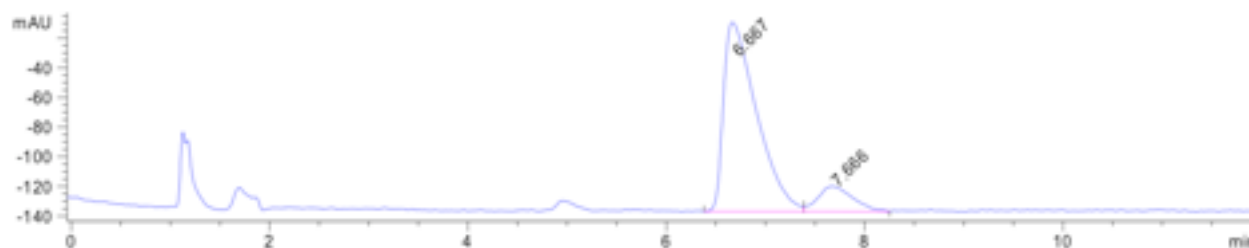
**rac-SI-17**

Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.050	VV	0.2814	576.97528	29.59732	49.1807
2	7.909	VB	0.3027	596.19904	26.47661	50.8193

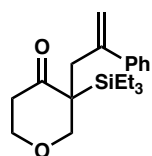


SI-17

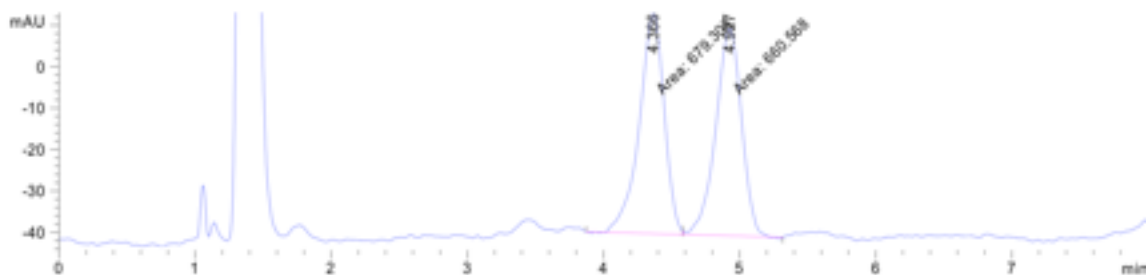


Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.667	BV	0.3324	2952.77930	127.38860	87.7272
2	7.666	VV	0.2993	413.08606	17.01272	12.2728



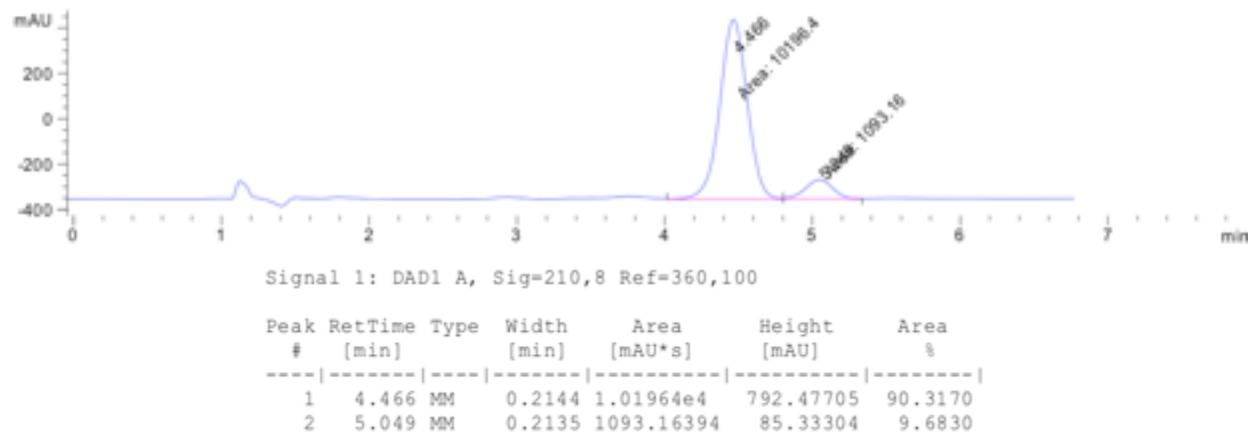
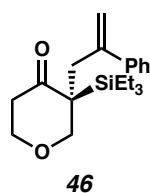
rac-46



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

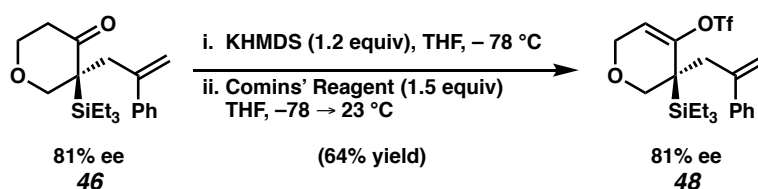
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.366	MF	0.2166	696.71619	53.61436	50.7874
2	4.927	FM	0.2232	675.11218	50.40852	49.2126





## G. Enantiospecific trappings

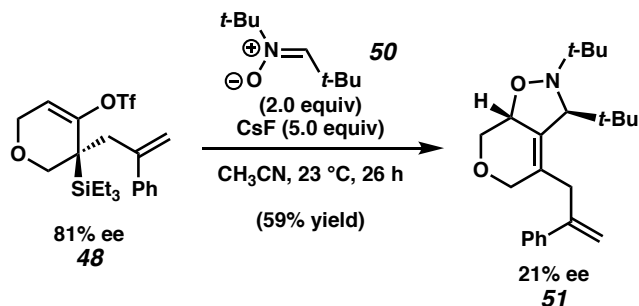
### Preparation of Silyl Triflate 48



**Silyl triflate 48.** To a solution of KHMDS (7.31 mg, 0.0367 mmol, 1.20 equiv) in THF (0.1 mL) at  $-78\text{ }^\circ\text{C}$  was added silyl ketone **46** (10.1 mg, 0.0306 mmol, 1.00 equiv) in THF (0.1 mL) dropwise over 1 min. The solution was stirred for 1 h at  $-78\text{ }^\circ\text{C}$ , before a solution of Comins' Reagent (18.0 mg, 0.0458 mmol, 1.50 equiv) in THF (0.1 mL) was added dropwise over 30 sec. Following the addition, the cooling bath was removed and the reaction was allowed to stir at  $23\text{ }^\circ\text{C}$ . After stirring for 11 h, the reaction was quenched with sat. aq.  $\text{NaHCO}_3$  (1.0 mL). The layers were then separated and the aqueous layer was extracted with EtOAc (3 x 4 mL). The combined organic layers were dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The resulting crude oil was purified by preparative thin layer chromatography (9:1 hexanes:EtOAc) to afford silyl triflate **48** as a colorless oil (15.0 mg, 64% yield, 81% ee). Silyl Triflate **48**:  $R_f$  0.48 (9:1 hexanes:EtOAc);  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.36–7.22 (m, 5H), 5.49 (app t,  $J = 5.8$ , 1H), 5.23 (d,  $J = 1.1$ , 1H), 5.13 (s, 1H), 3.97 (d,  $J = 3.0$ , 2H), 3.72 (d,  $J =$

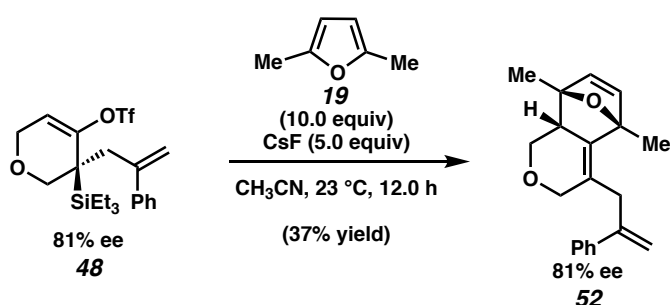
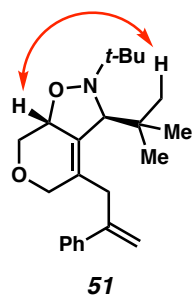
11.8, 1H), 3.54 (d,  $J = 11.8$ , 1H), 3.02 (d,  $J = 14.2$ , 1H), 2.68 (d,  $J = 14.2$ , 1H), 1.02 (t,  $J = 7.9$ , 9H), 0.72 (q,  $J = 7.9$ , 6H);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  151.3, 146.4, 143.4, 142.7, 128.2, 126.7, 118.4 (q,  $J = 320$ ), 117.1, 110.7, 70.2, 64.2, 36.5, 36.3, 8.1, 2.6;  $^{19}\text{F}$ -NMR (376 Hz,  $\text{CDCl}_3$ ):  $-74.9$ ; IR (film): 2955, 2878, 1739, 1366, 1216  $\text{cm}^{-1}$ ;  $[\alpha]^{26.3}_{\text{D}} -4.00^\circ$  ( $c = 1.00$ ,  $\text{CH}_2\text{Cl}_2$ ).

**Representative Procedure (Preparation of cycloadduct **51** is used as an example).**



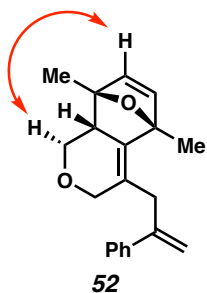
**Isoxazolidine **51**.** To a stirred solution of silyl triflate **48** (14.2 mg, 0.031 mmol, 1.0 equiv) and nitronium **50** (9.7 mg, 0.0614 mmol, 2.0 equiv) in  $\text{CH}_3\text{CN}$  (0.30 mL) was added CsF (23.3 mg, 0.153 mmol, 5.0 equiv). The reaction vessel was sealed and allowed to stir at  $23^\circ\text{C}$  for 26 h. The reaction mixture was filtered by passage through a plug of silica gel (EtOAc eluent, 15 mL). Concentration under reduced pressure yielded the crude residue (1.6:1 dr). Purification by preparative thin layer chromatography (1:1 hexanes: $\text{CH}_2\text{Cl}_2$ ) allowed for separation of the two diastereomers, which were obtained in a total yield of 59%. The major diastereomer **51** was obtained as a colorless oil (21% ee). Isoxazolidine **51**:  $R_f$  0.12 (9:1 hexanes:EtOAc);  $^1\text{H}$ -NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.40–7.20 (m, 5H), 5.38 (d,  $J = 0.7$ , 1H), 5.30 (s, 1H), 5.13–5.11 (m, 1H), 4.40–4.34 (m, 1H), 4.23–4.17 (m, 2H), 3.82 (dd,  $J = 16.2$ , 2.9, 1H), 3.54 (s, 1H), 3.30 (s, 2H), 3.16 (app t,  $J = 9.6$ , 1H), 0.98 (s, 9H), 0.97 (s, 9H);  $^{13}\text{C}$ -NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  144.4, 141.5, 137.4, 128.5, 127.8, 126.1, 125.8, 115.0, 71.7, 67.7, 67.4, 67.2, 59.5, 53.4, 37.0, 36.0, 27.8, 26.9; IR (film): 2954, 1738, 1445, 1363, 1217, 1096  $\text{cm}^{-1}$ ; HRMS–APCI ( $m/z$ )  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{23}\text{H}_{33}\text{NO}_2^+$ , 355.25058; found, 355.25071.  $[\alpha]^{29.5}_{\text{D}} -4.00^\circ$  ( $c = 1.00$ ,  $\text{CH}_2\text{Cl}_2$ ).

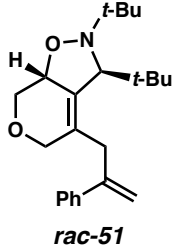
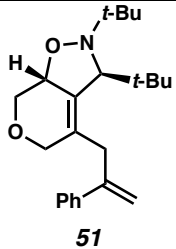
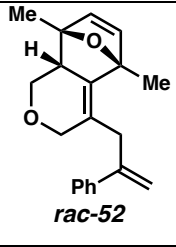
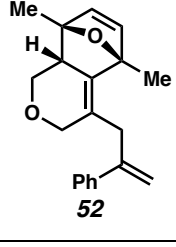
The structure of **51** was verified by 2D-NOESY, as the following interaction was observed:

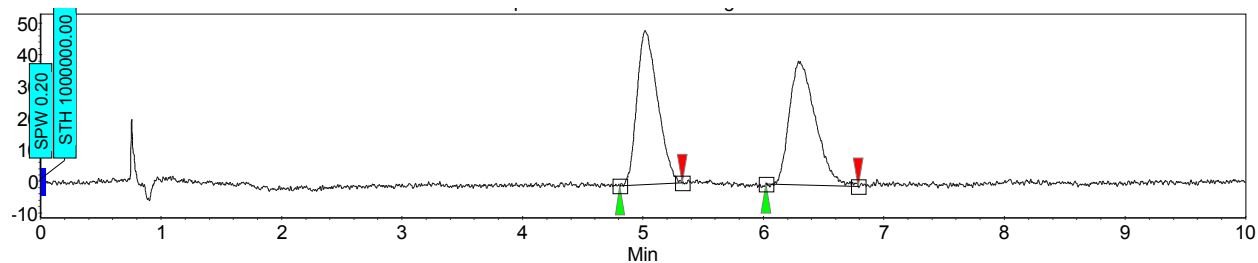
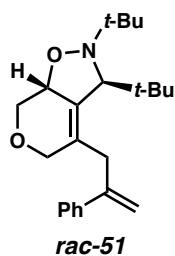


**Cycloadduct 52.** Following concentration under reduced pressure, the crude residue was obtained (>20:1 dr). Purification by preparative thin layer chromatography (5:1 hexanes:EtOAc) afforded cycloadduct **52** as a colorless oil in 37% yield (81% ee). Cycloadduct **52**:  $R_f$  0.35 (9:1 hexanes:EtOAc);  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.42–7.38 (m, 2H), 7.36–7.27 (m, 3H), 6.17 (d,  $J = 5.4$ , 1H), 5.85 (d,  $J = 5.4$ , 1H), 5.39–5.37 (m, 1H), 5.09–5.06 (m, 1H), 4.13–4.06 (m, 2H), 3.82 (dd,  $J = 10.1$ , 2.8, 1H), 3.30 (d,  $J = 16.7$ , 1H), 3.15 (d,  $J = 16.7$ , 1H), 2.51–2.46 (m, 1H), 2.40 (dd,  $J = 10.6$ , 9.3, 1H), 1.76 (s, 3H), 1.62 (s, 3H);  $^{13}\text{C-NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  145.4, 141.3, 139.8, 138.6, 133.5, 128.4, 127.7, 125.9, 123.4, 113.7, 87.4, 85.7, 67.3, 67.2, 46.7, 34.2, 18.2, 17.5; IR (film): 2924, 2852, 1741, 1632, 1380  $\text{cm}^{-1}$ ; HRMS–APCI ( $m/z$ )  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{20}\text{H}_{23}\text{O}_2^+$ , 295.16926; found, 295.17032.  $[\alpha]_D^{28.6} +73.3^\circ$  ( $c = 1.00$ ,  $\text{CH}_2\text{Cl}_2$ ).

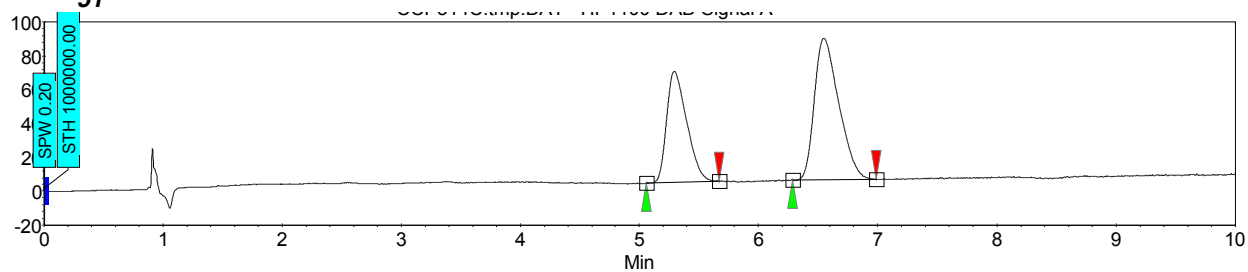
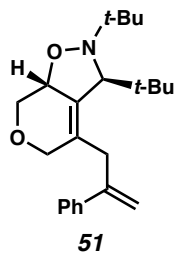
The structure of **52** was verified by 2D-NOESY, as the following interaction was observed:



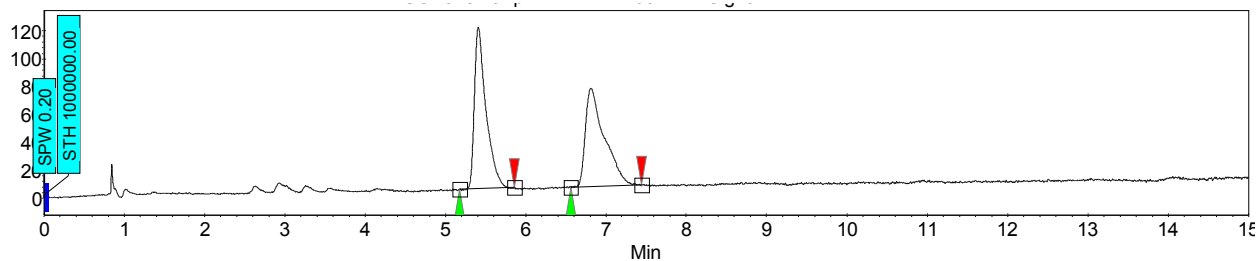
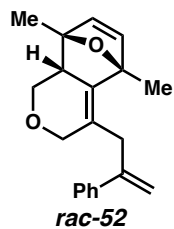
Compound	Method Column/Temp.	Solvent	Method Flow Rate	Retention Times (min)	Enantiomeric Ratio (er)
 <b>rac-51</b>	ChiralPak IC-3/35°C	5% isopropanol in CO <sub>2</sub>	3.5 mL/min	5.02/6.29	49.7/50.3
 <b>51</b>	ChiralPak IC-3/35°C	5% isopropanol in CO <sub>2</sub>	3.5 mL/min	5.29/6.55	39.2/60.8
 <b>rac-52</b>	ChiralPak AD-3/35°C	5% isopropanol in CO <sub>2</sub>	3.5 mL/min	5.41/6.80	49.9/50.1
 <b>52</b>	ChiralPak AD-3/35°C	5% isopropanol in CO <sub>2</sub>	3.5 mL/min	6.06/6.91	90.7/9.3



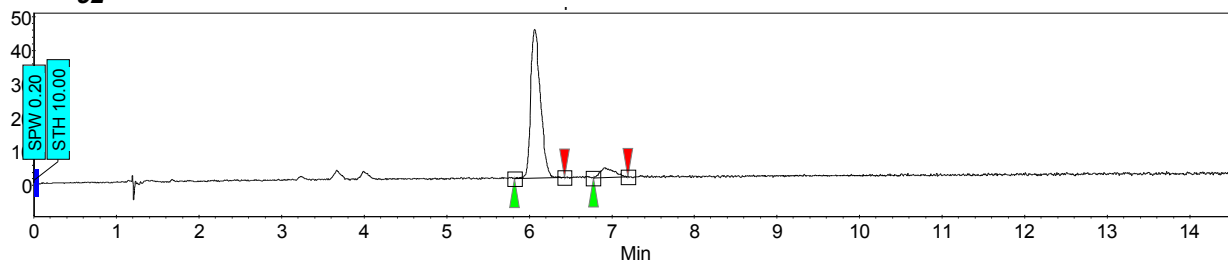
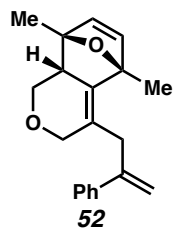
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μV]	[μV.Min]	[%]
1	UNKNOWN	4.81	5.02	5.33	0.00	49.74	48.7	9.7	49.742
2	UNKNOWN	6.02	6.29	6.79	0.00	50.26	39.3	9.8	50.258
Total						100.00	88.0	19.6	100.000



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μV]	[μV.Min]	[%]
1	UNKNOWN	5.06	5.29	5.67	0.00	39.25	65.6	12.8	39.249
2	UNKNOWN	6.28	6.55	6.99	0.00	60.75	83.3	19.7	60.751
Total						100.00	148.9	32.5	100.000



Index	Name	Start [Min]	Time [Min]	End [Min]	RT Offset [Min]	Quantity [% Area]	Height [μV]	Area [μV.Min]	Area [%]
1	UNKNOWN	5.17	5.41	5.86	0.00	49.86	115.6	19.3	49.859
2	UNKNOWN	6.56	6.80	7.45	0.00	50.14	70.3	19.4	50.141
Total						100.00	185.9	38.7	100.000



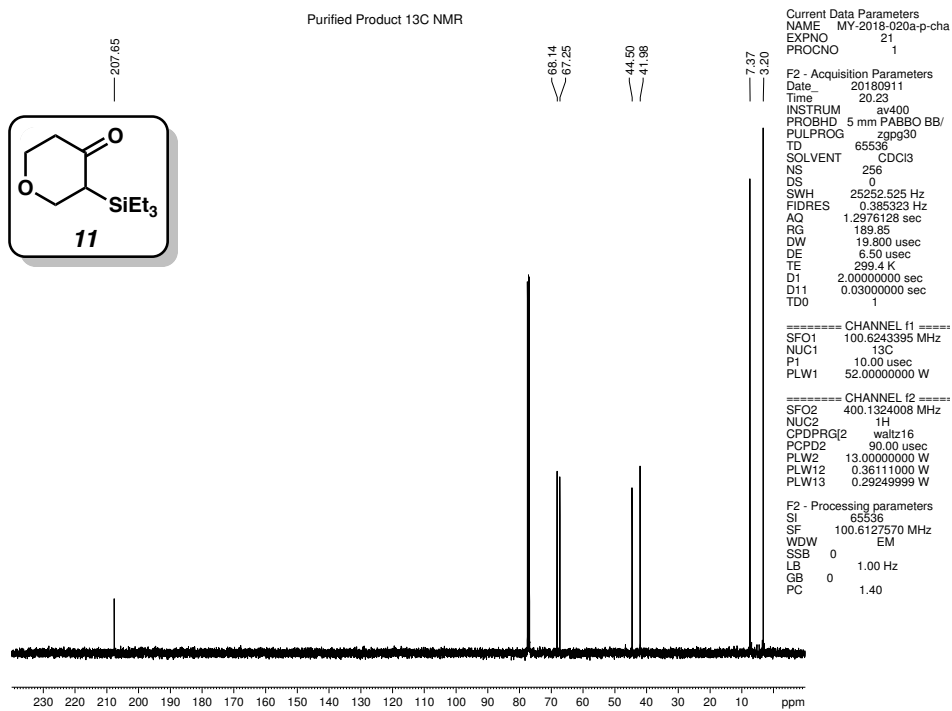
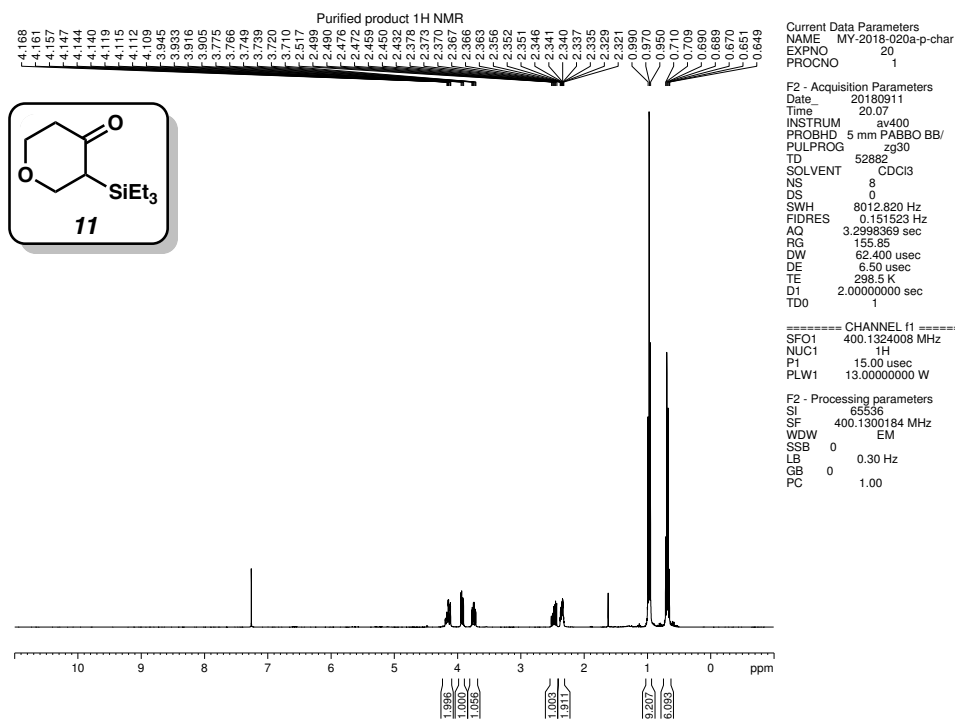
Index	Name	Start [Min]	Time [Min]	End [Min]	RT Offset [Min]	Quantity [% Area]	Height [μV]	Area [μV.Min]	Area [%]
1	UNKNOWN	5.82	6.06	6.42	0.00	90.73	44.0	6.0	90.732
2	UNKNOWN	6.77	6.91	7.20	0.00	9.27	3.0	0.6	9.268
Total						100.00	47.0	6.6	100.000

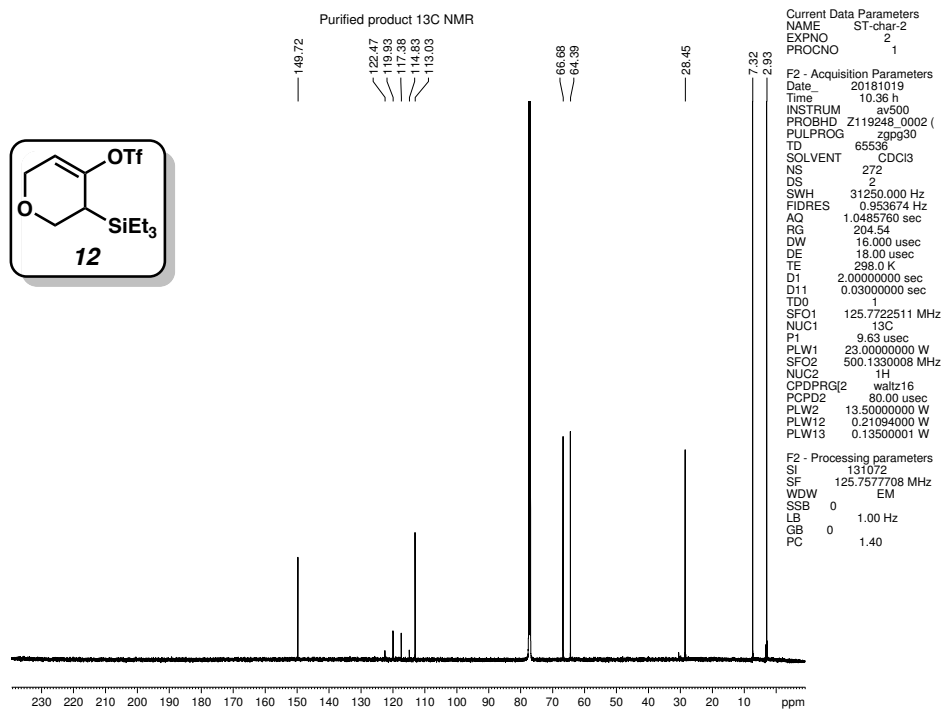
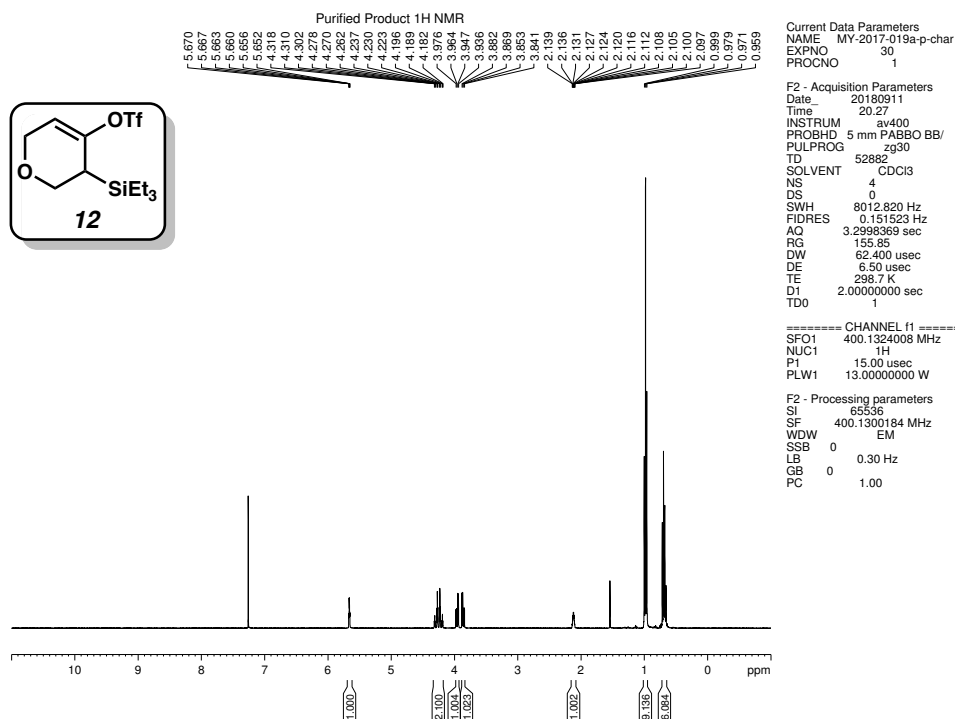
## References

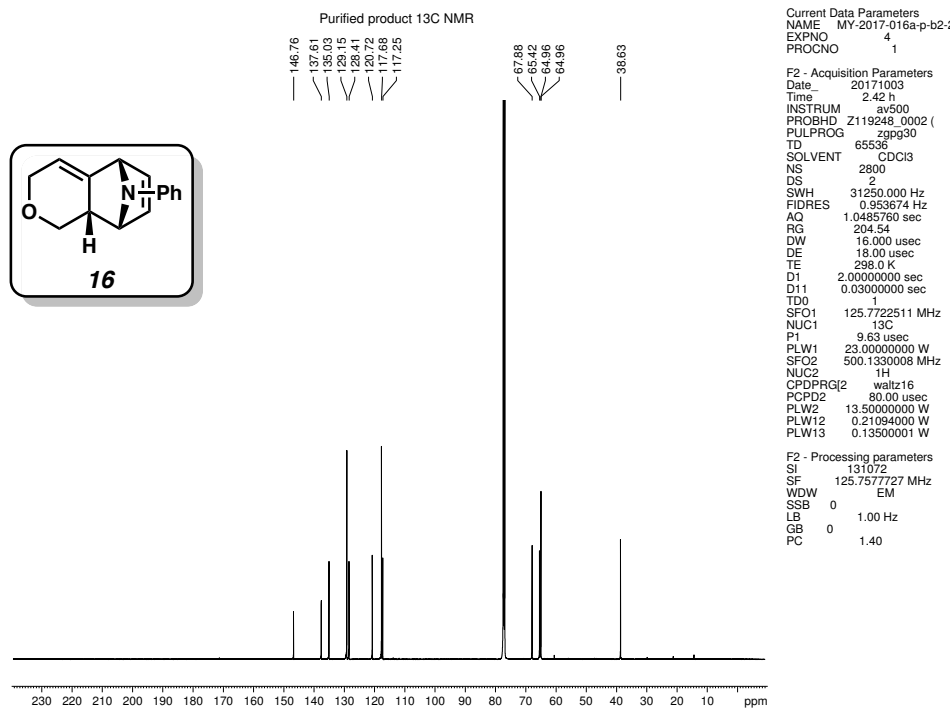
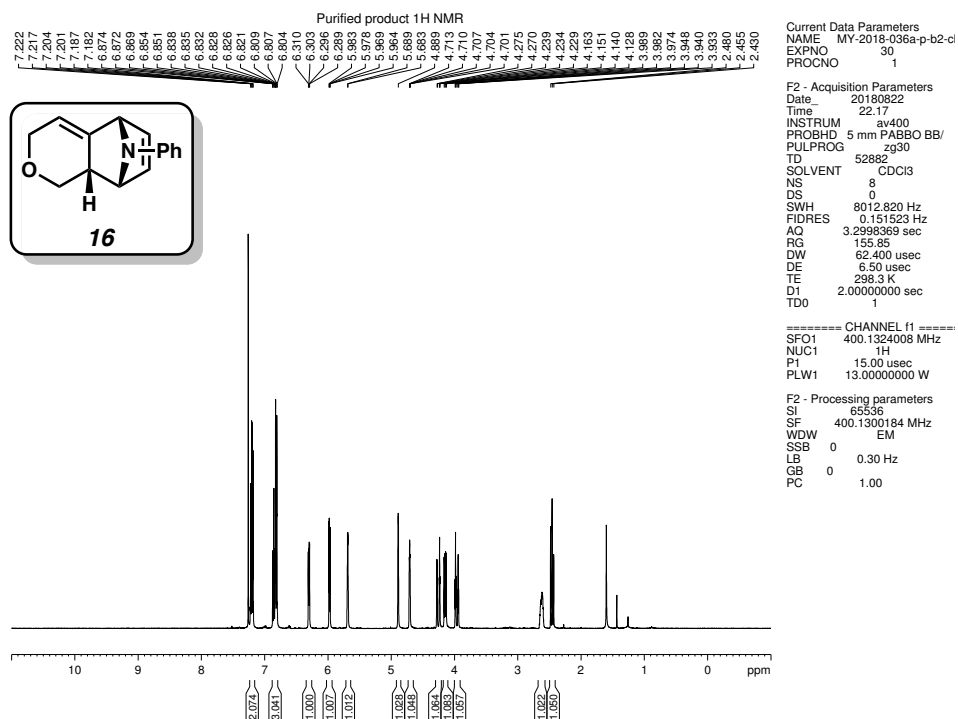
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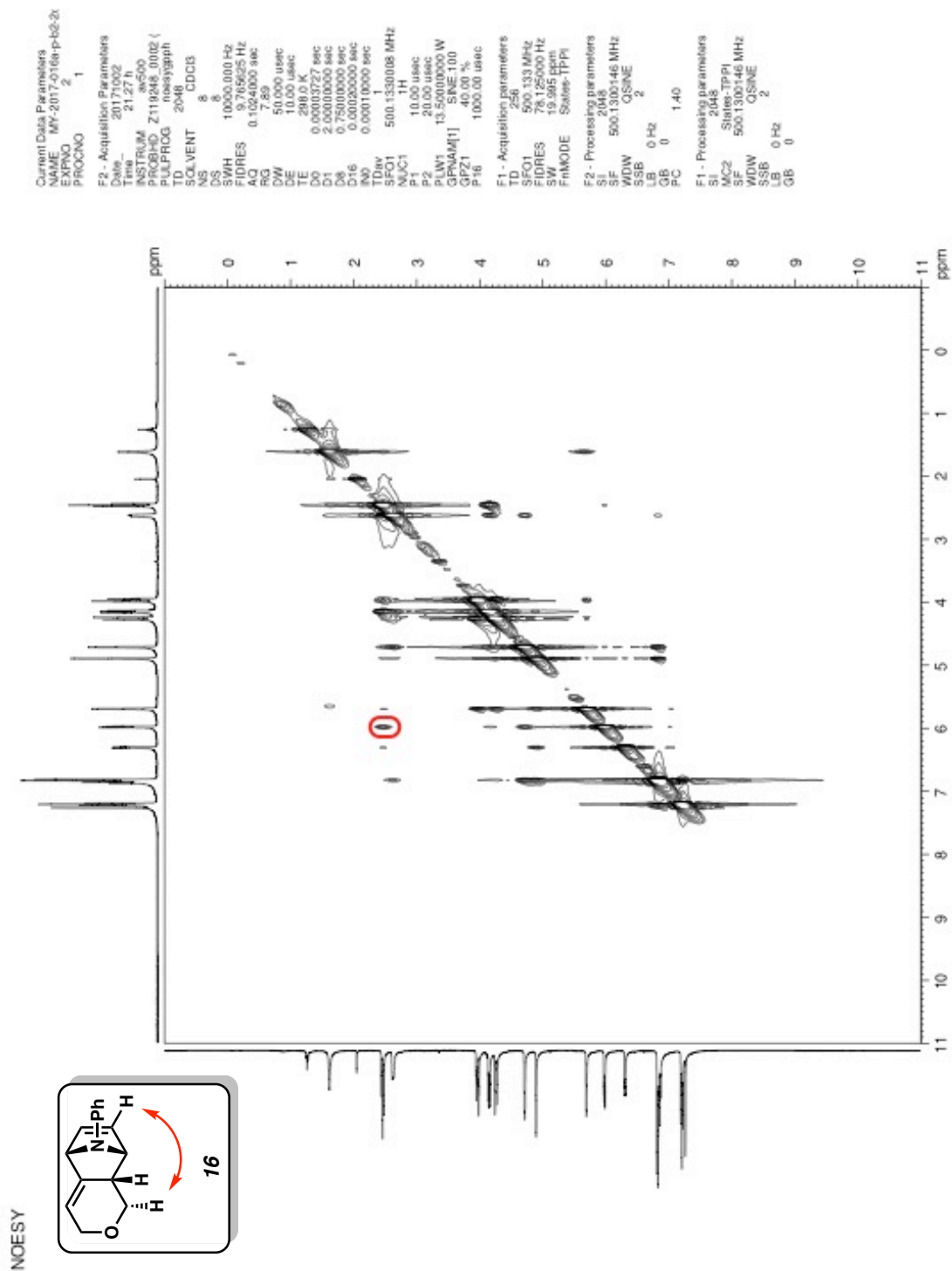
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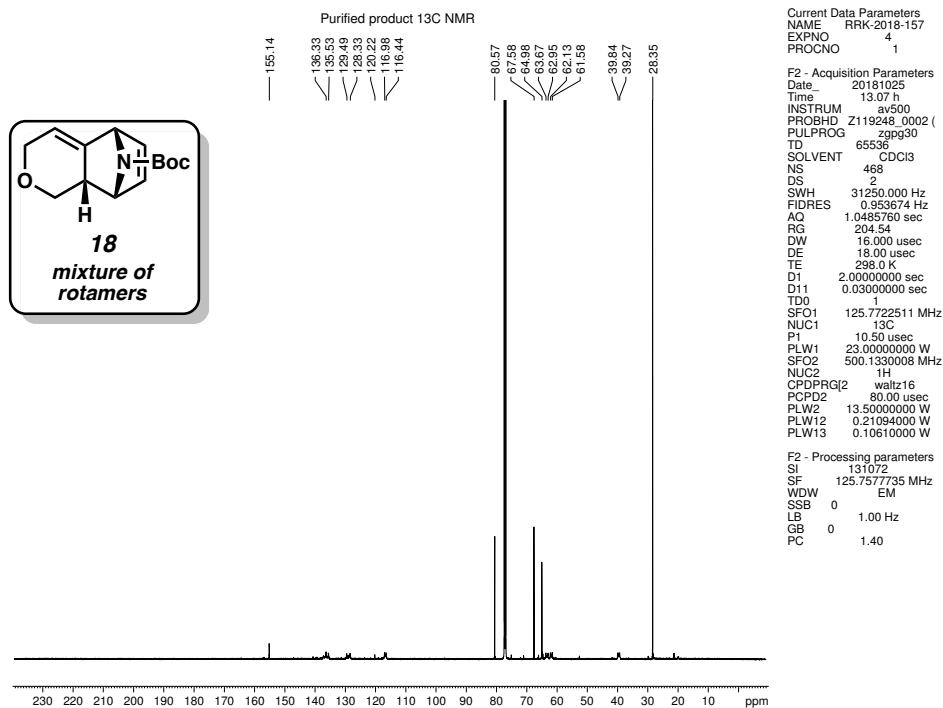
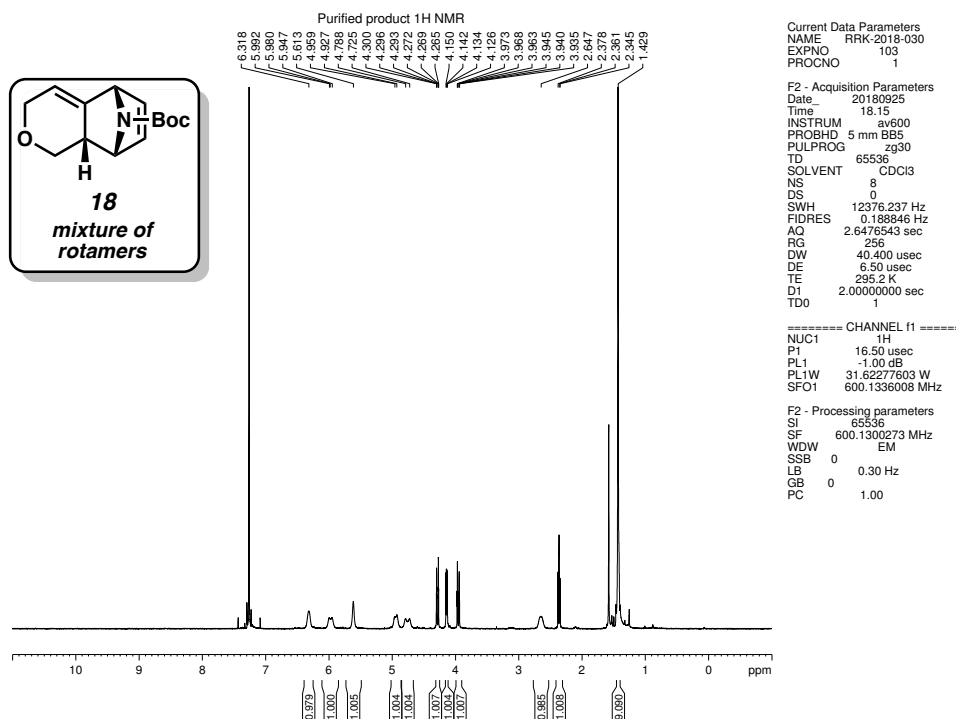


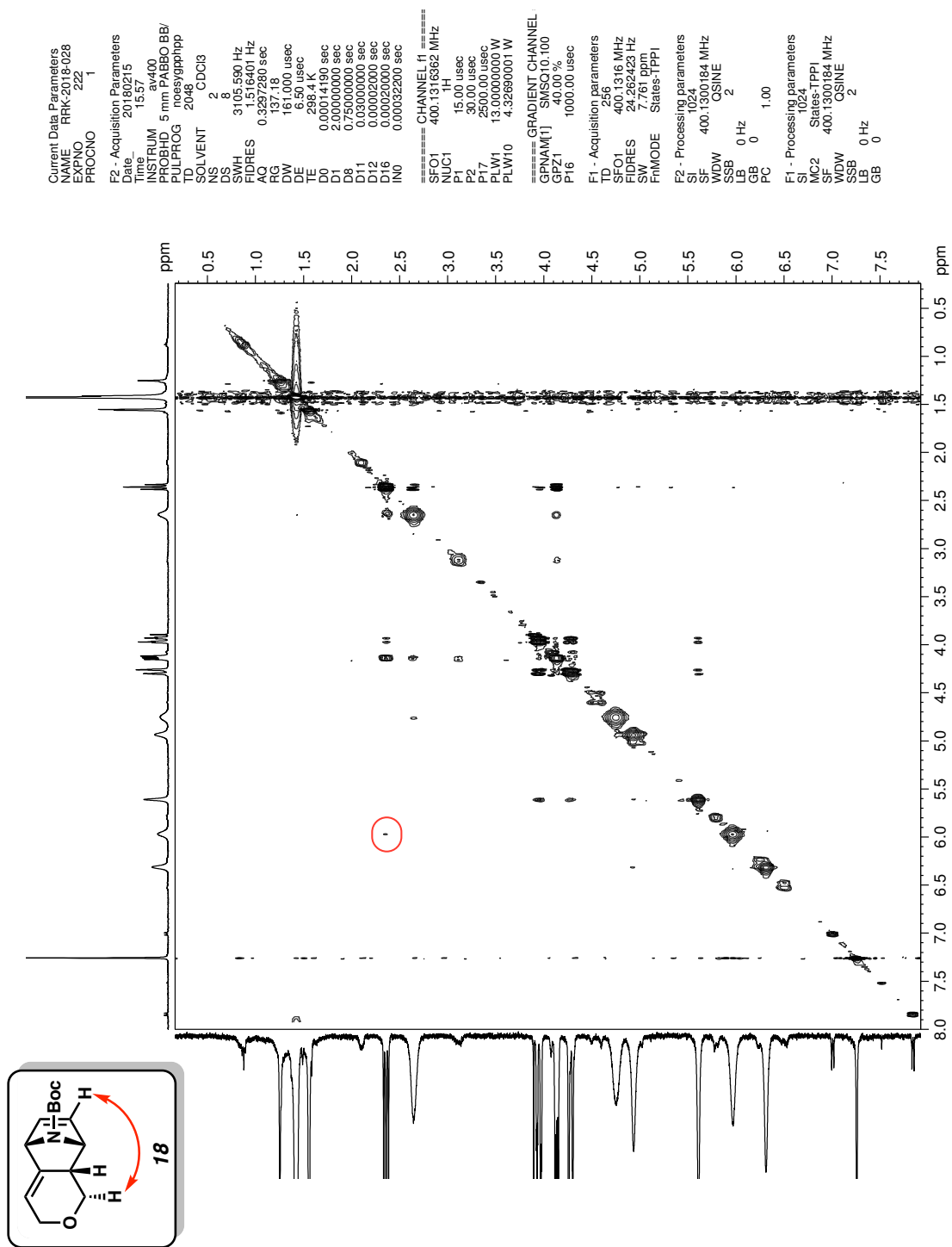


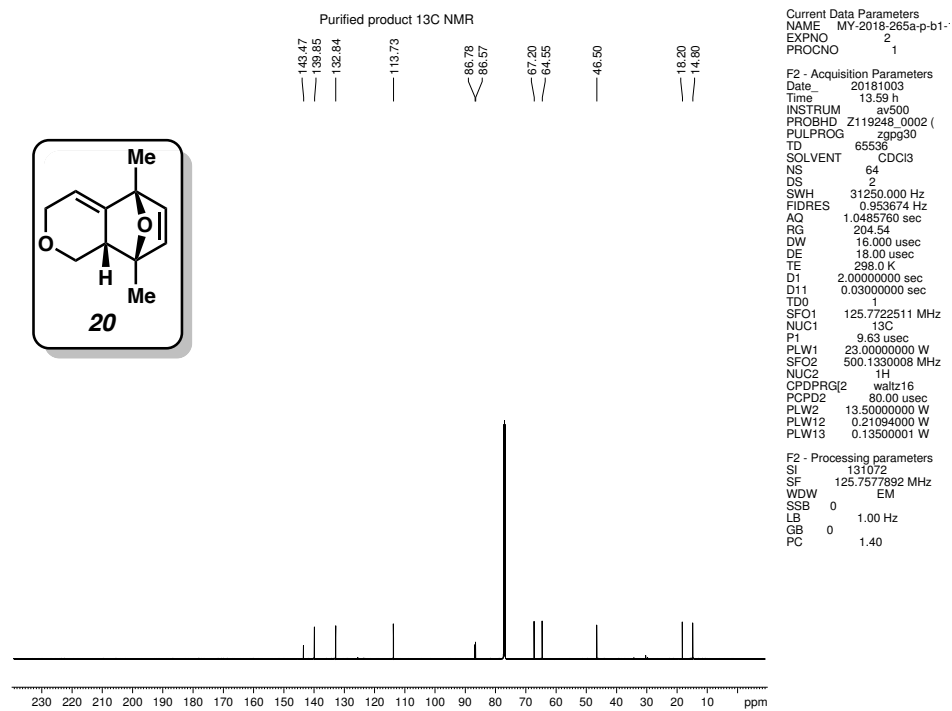
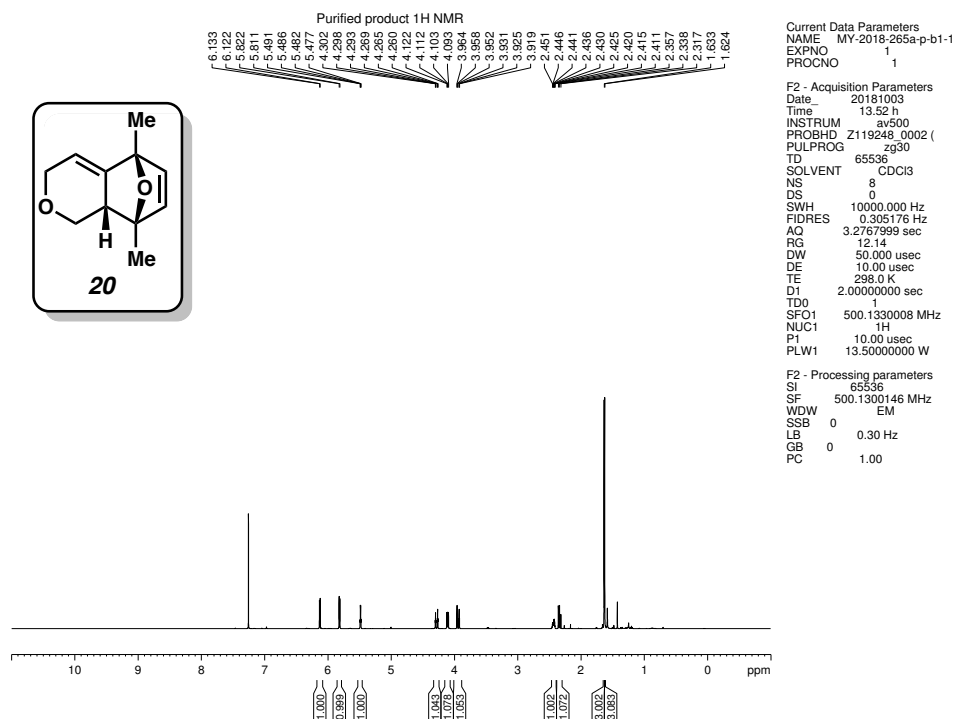


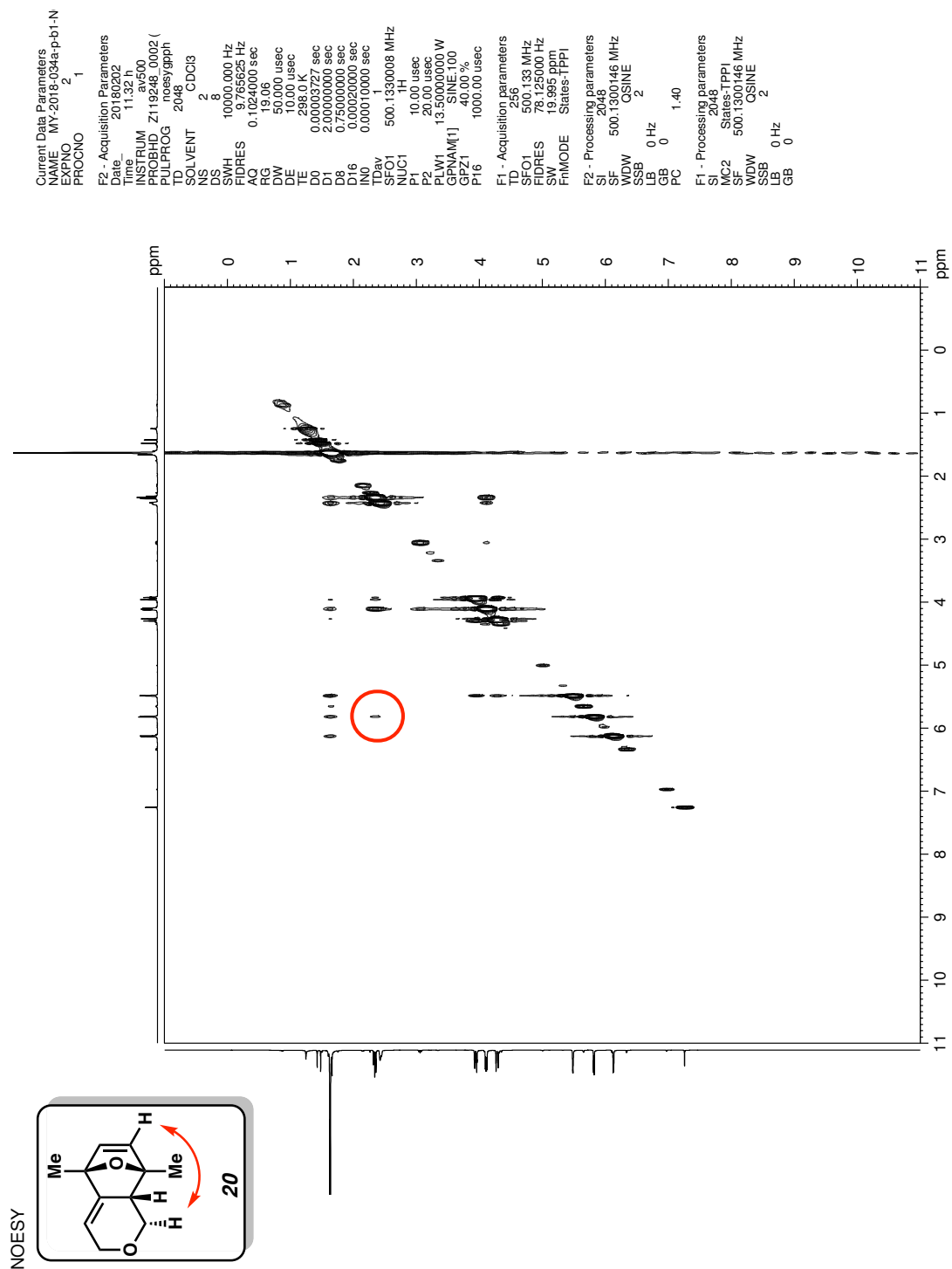




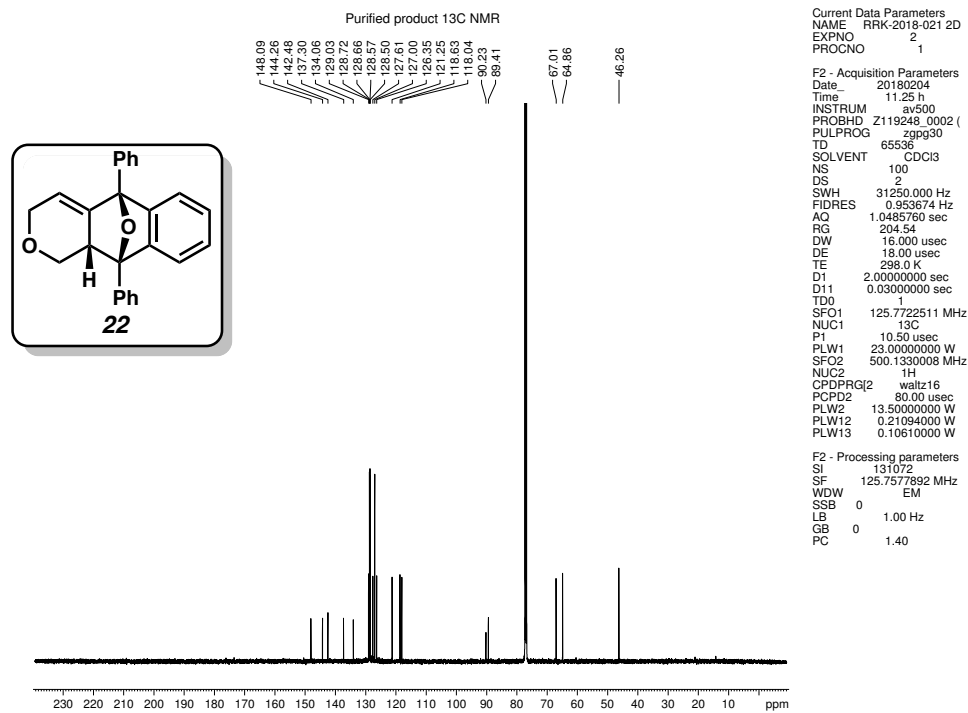
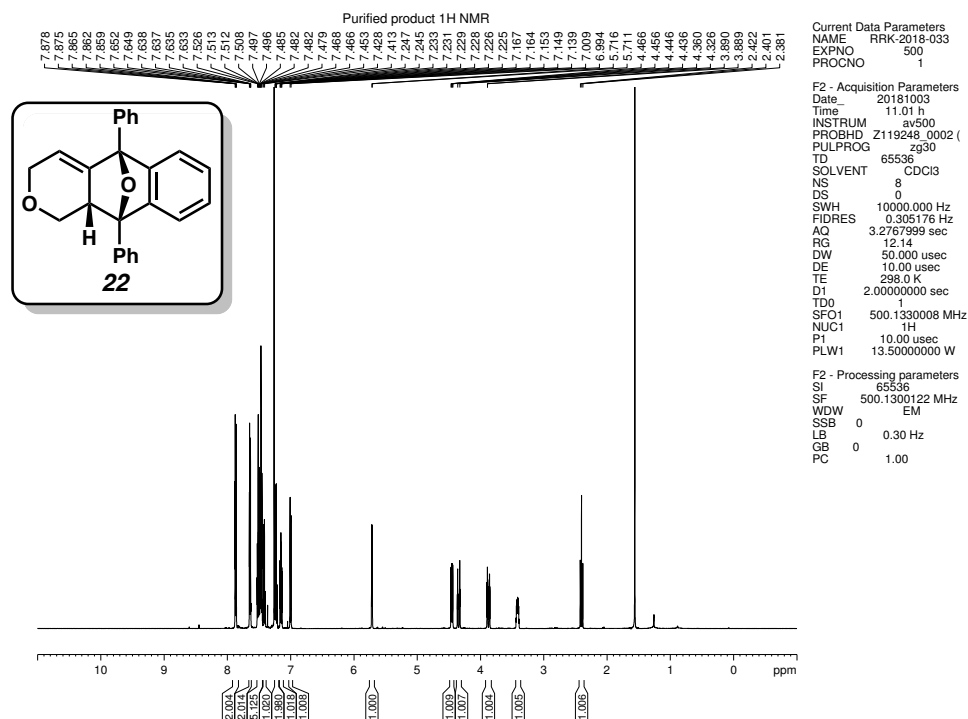


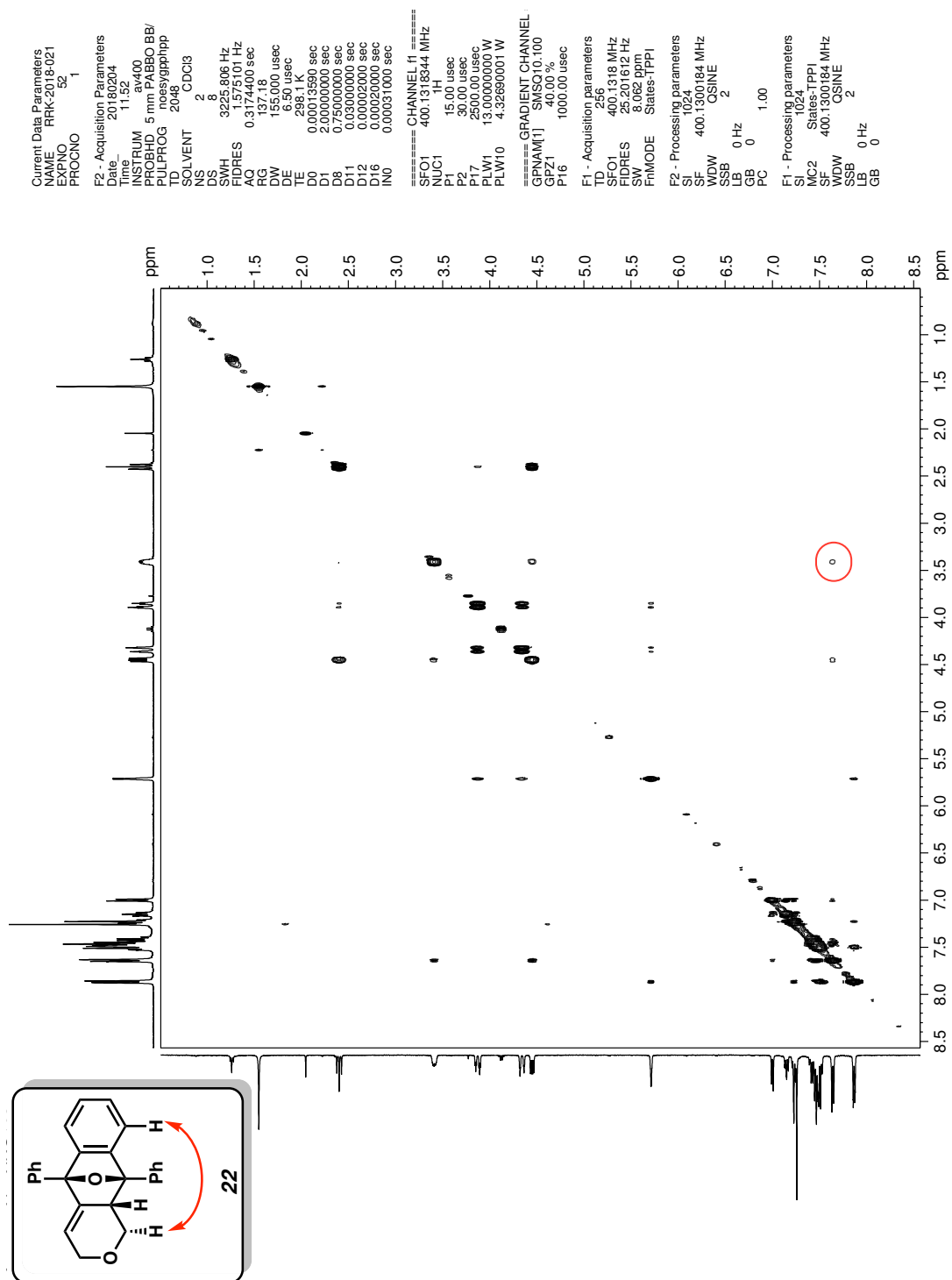


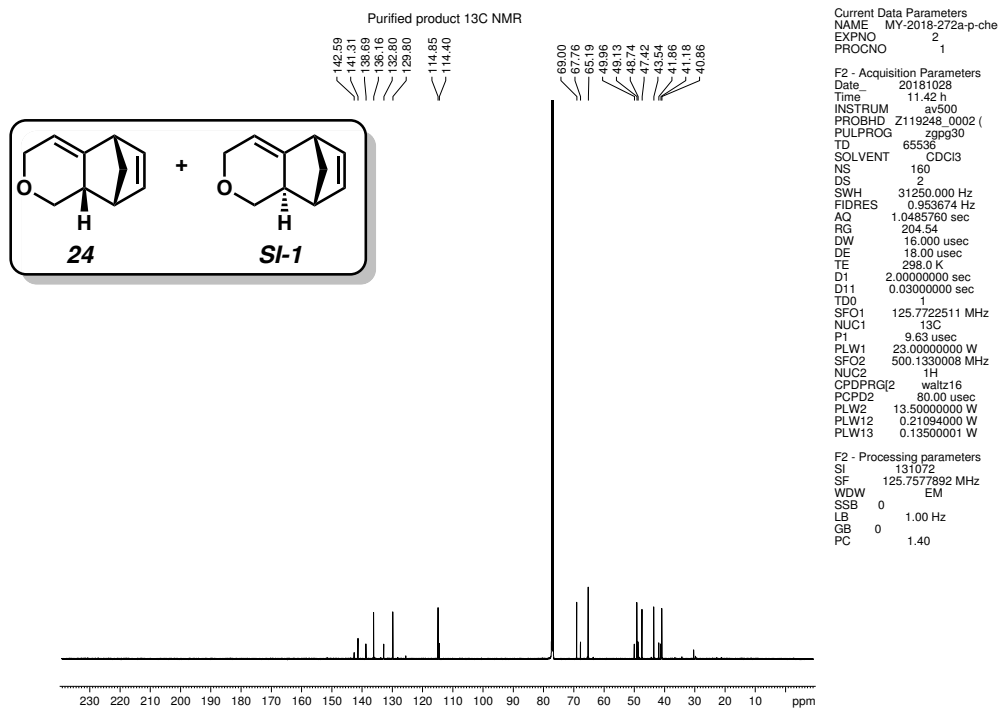
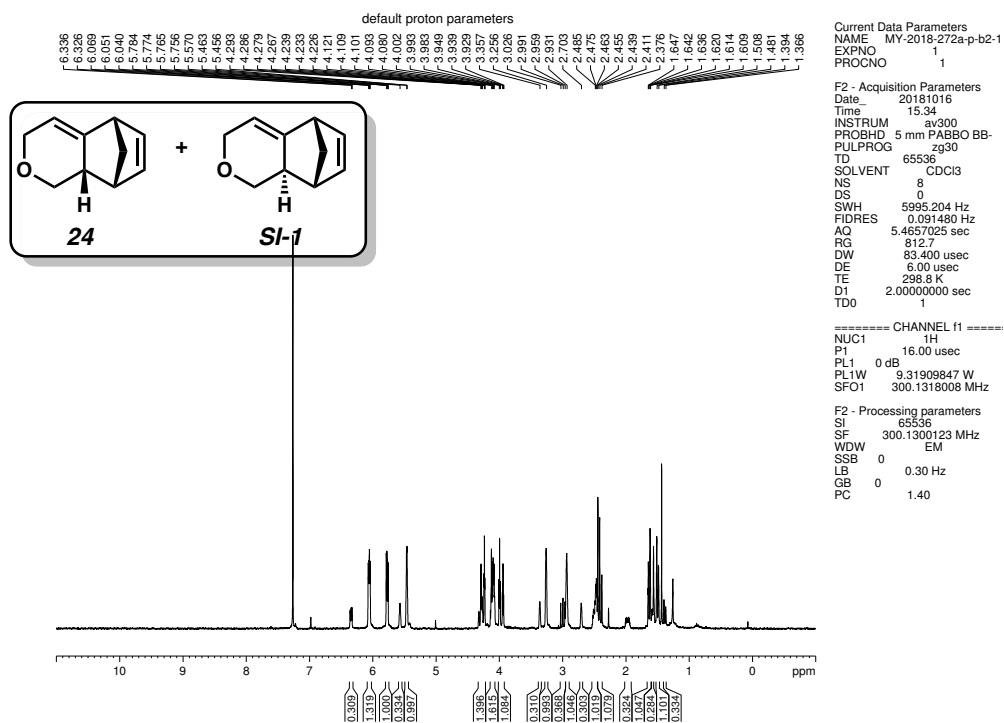


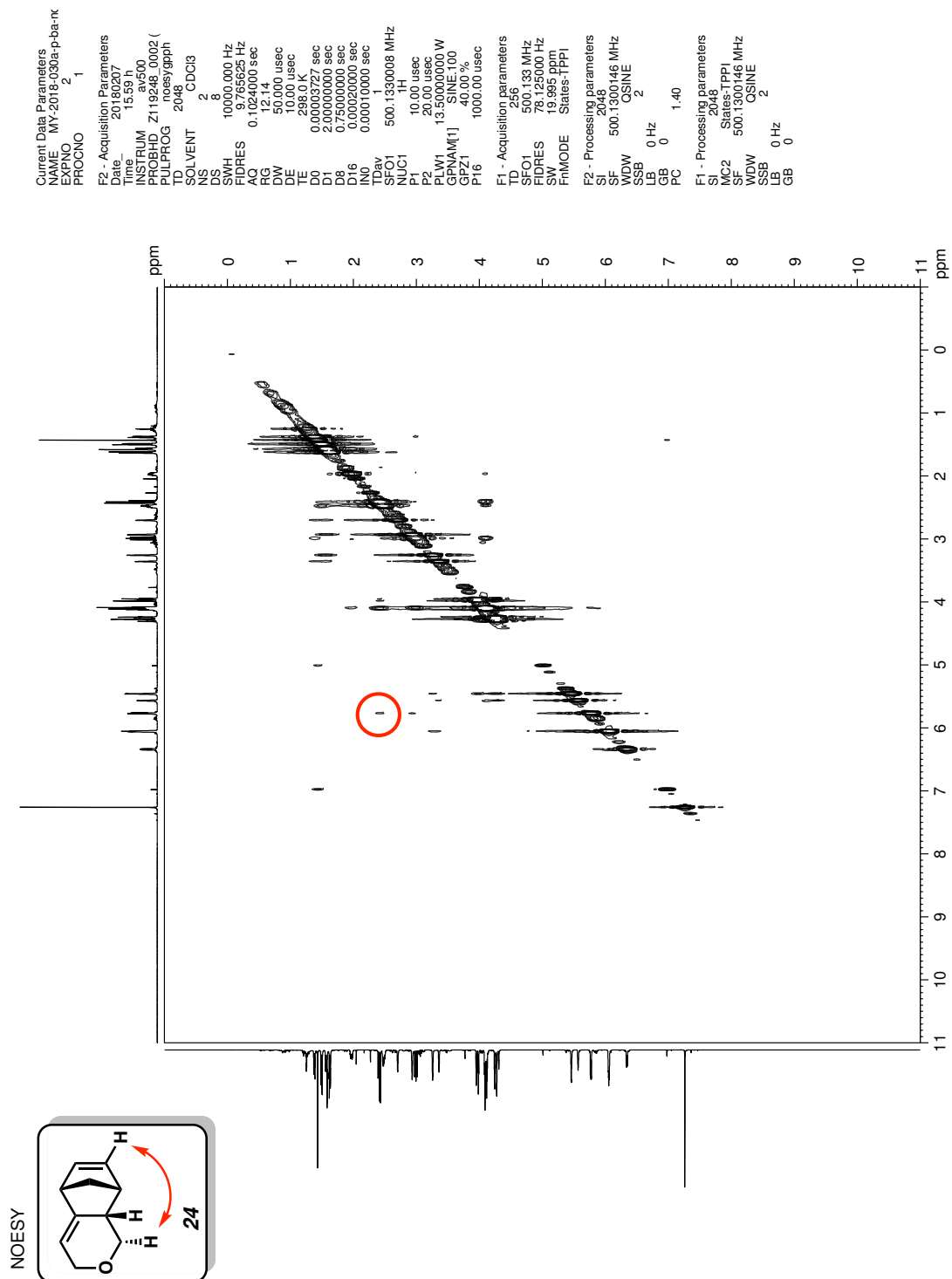


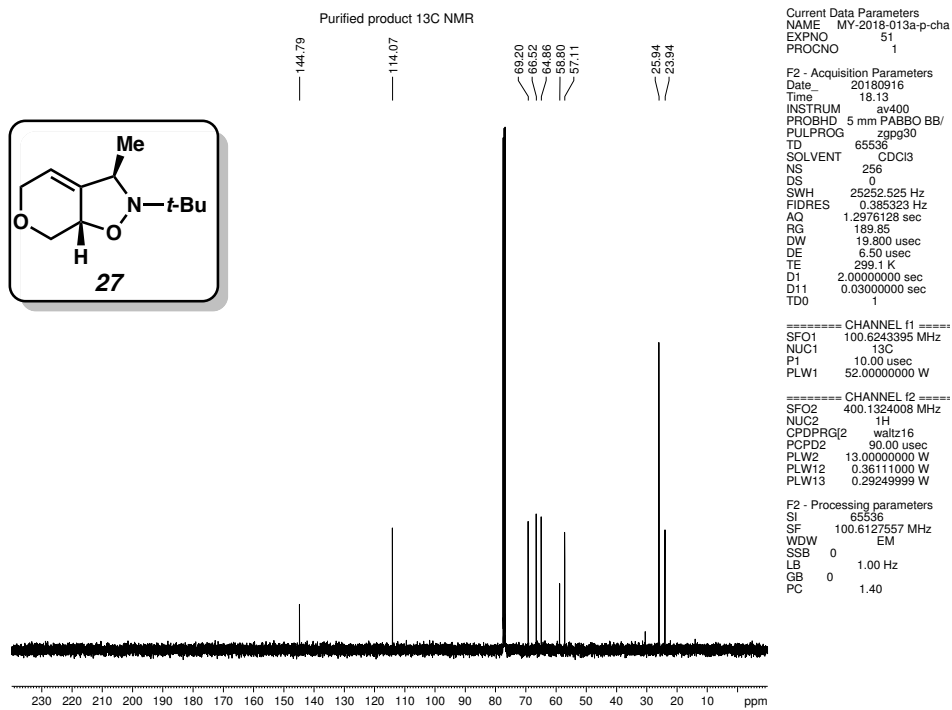
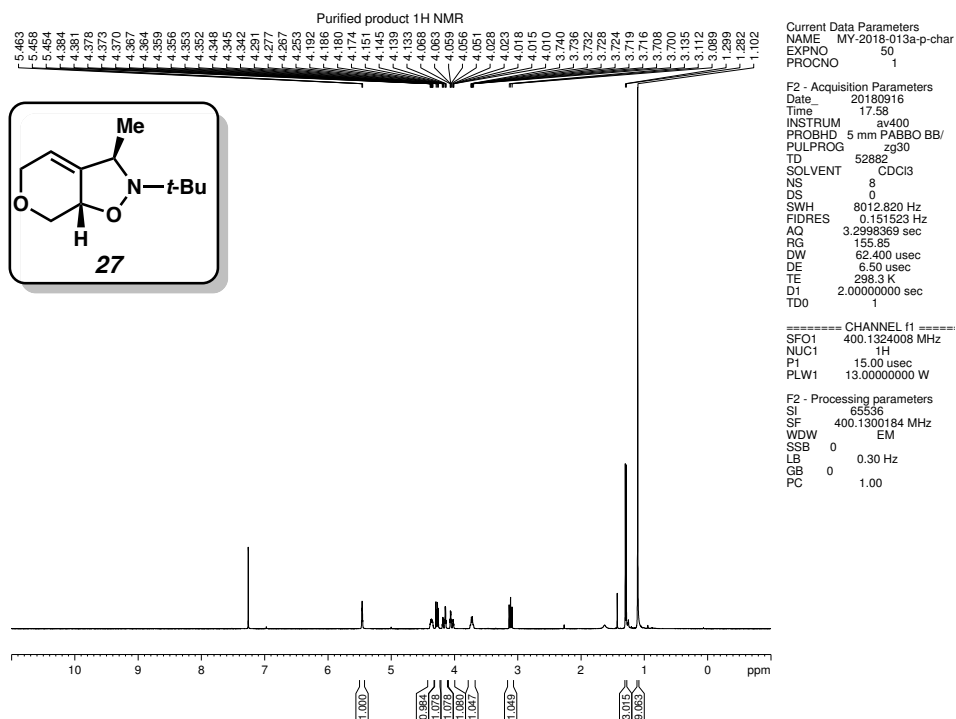


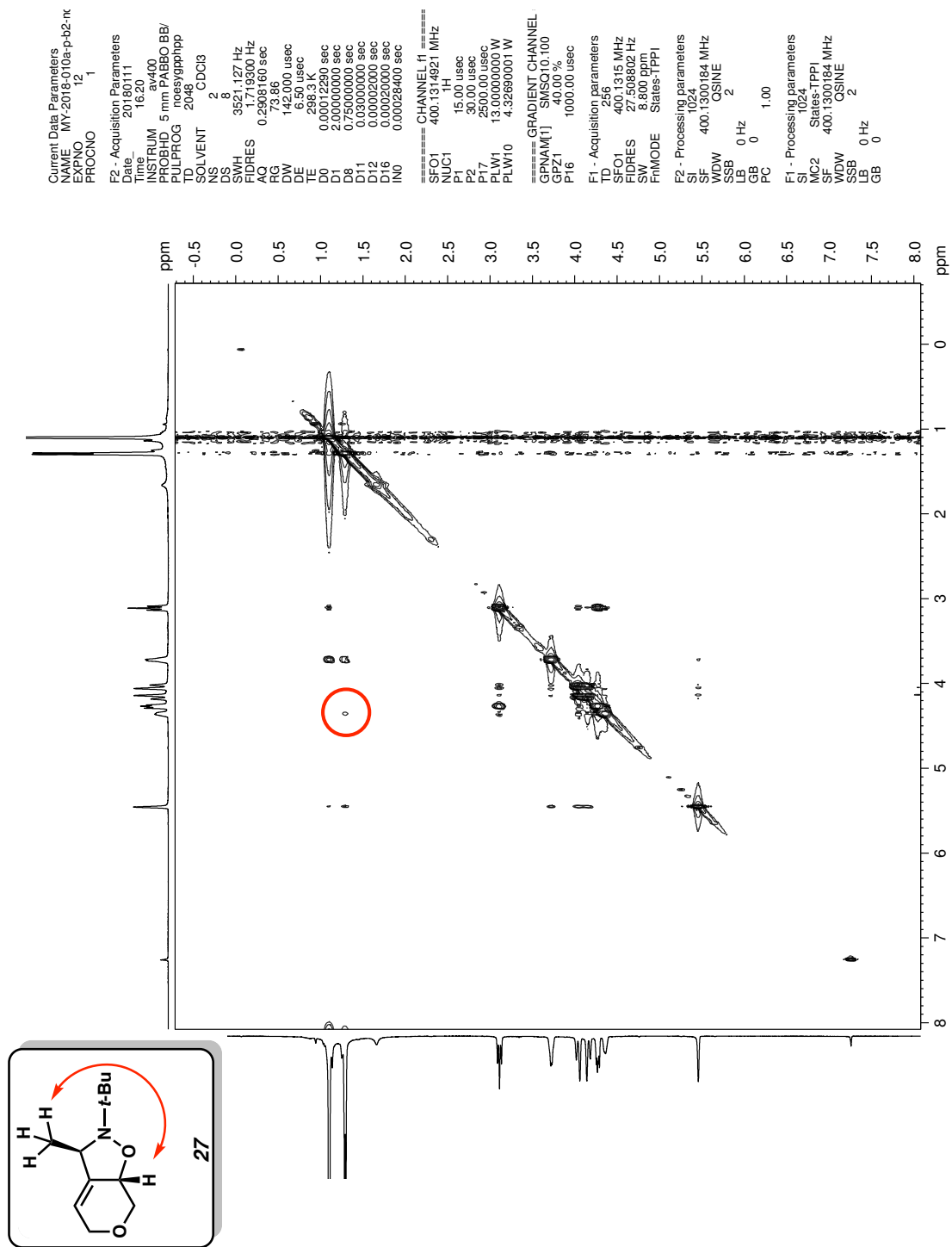


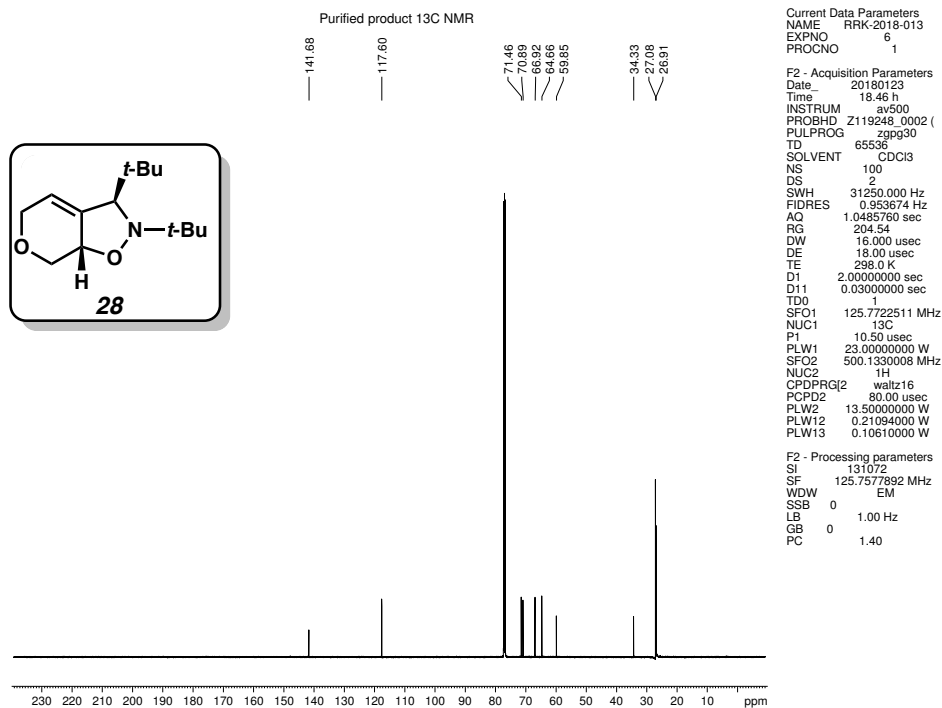
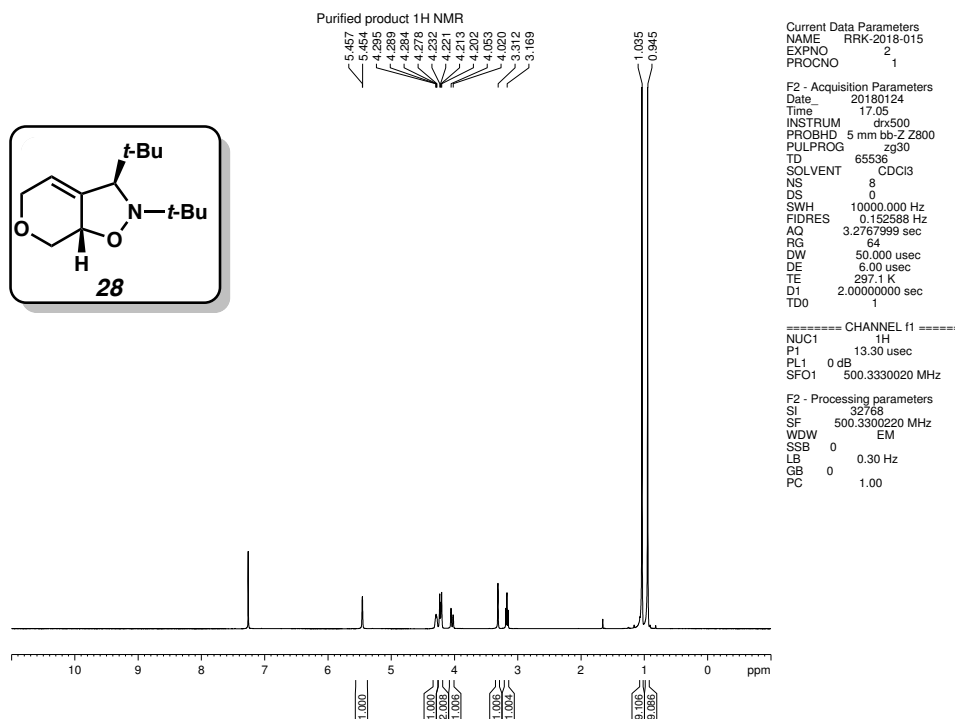


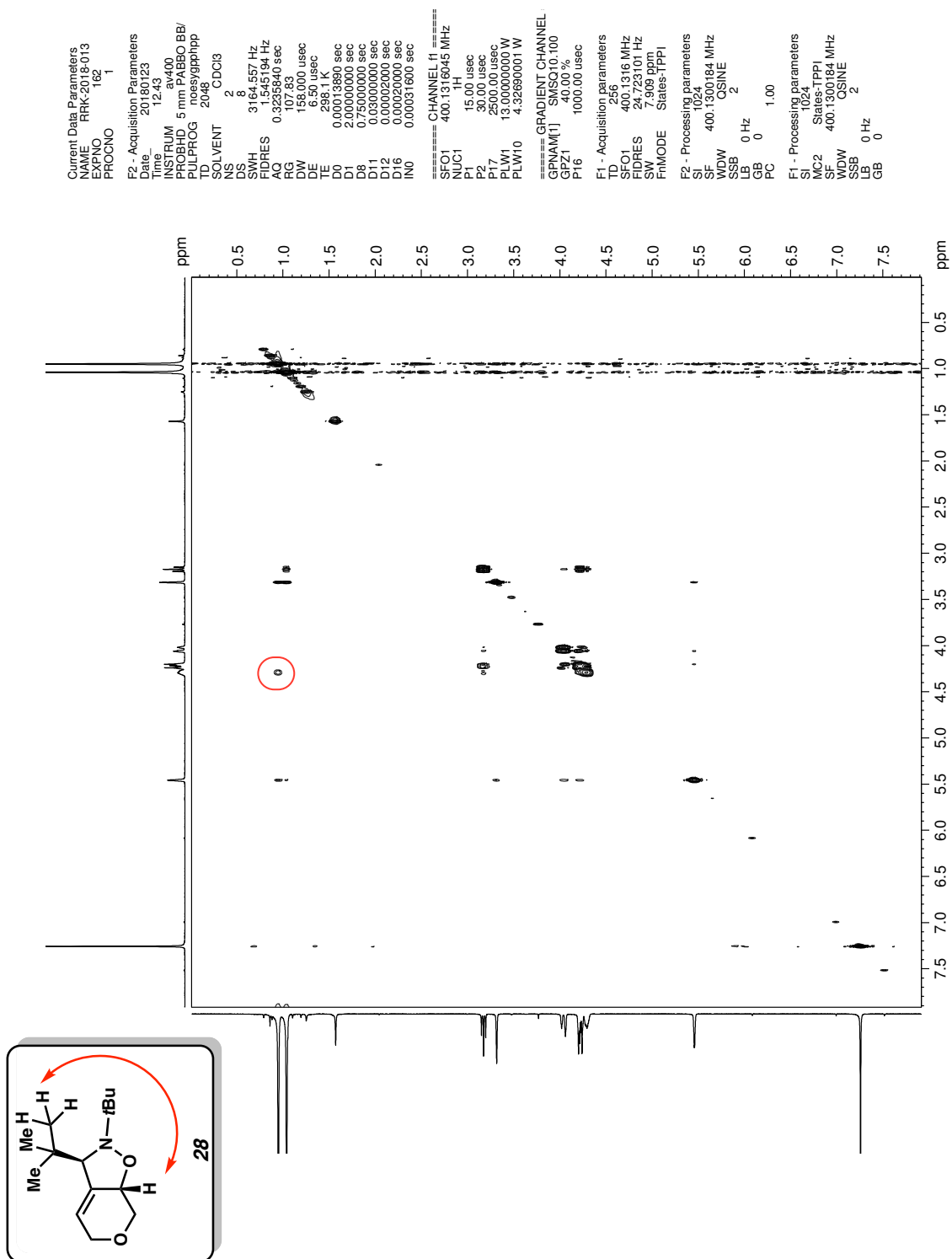




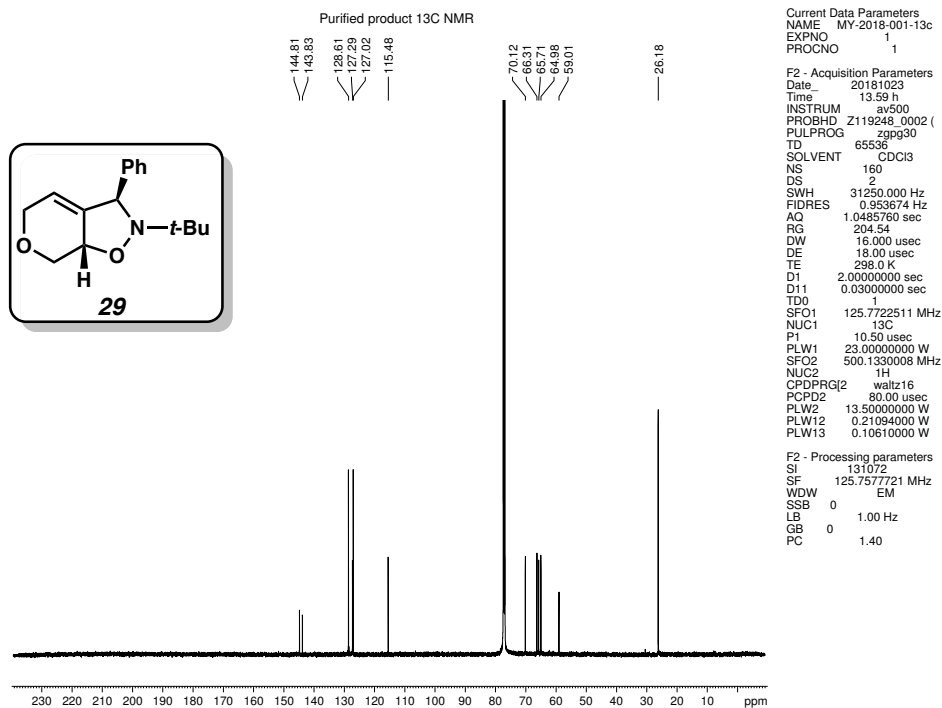
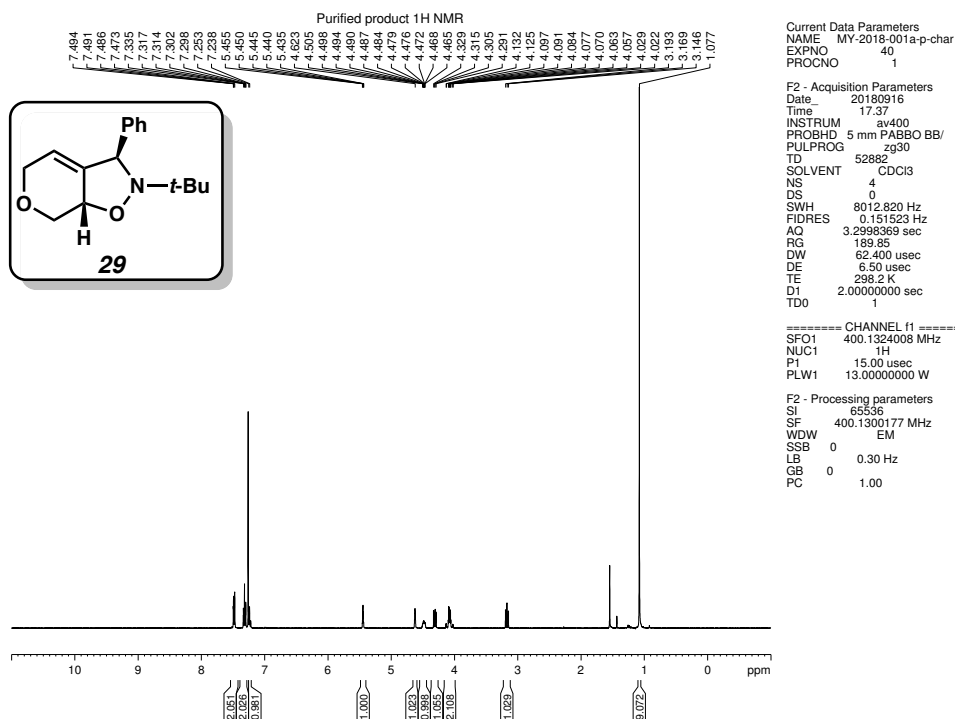


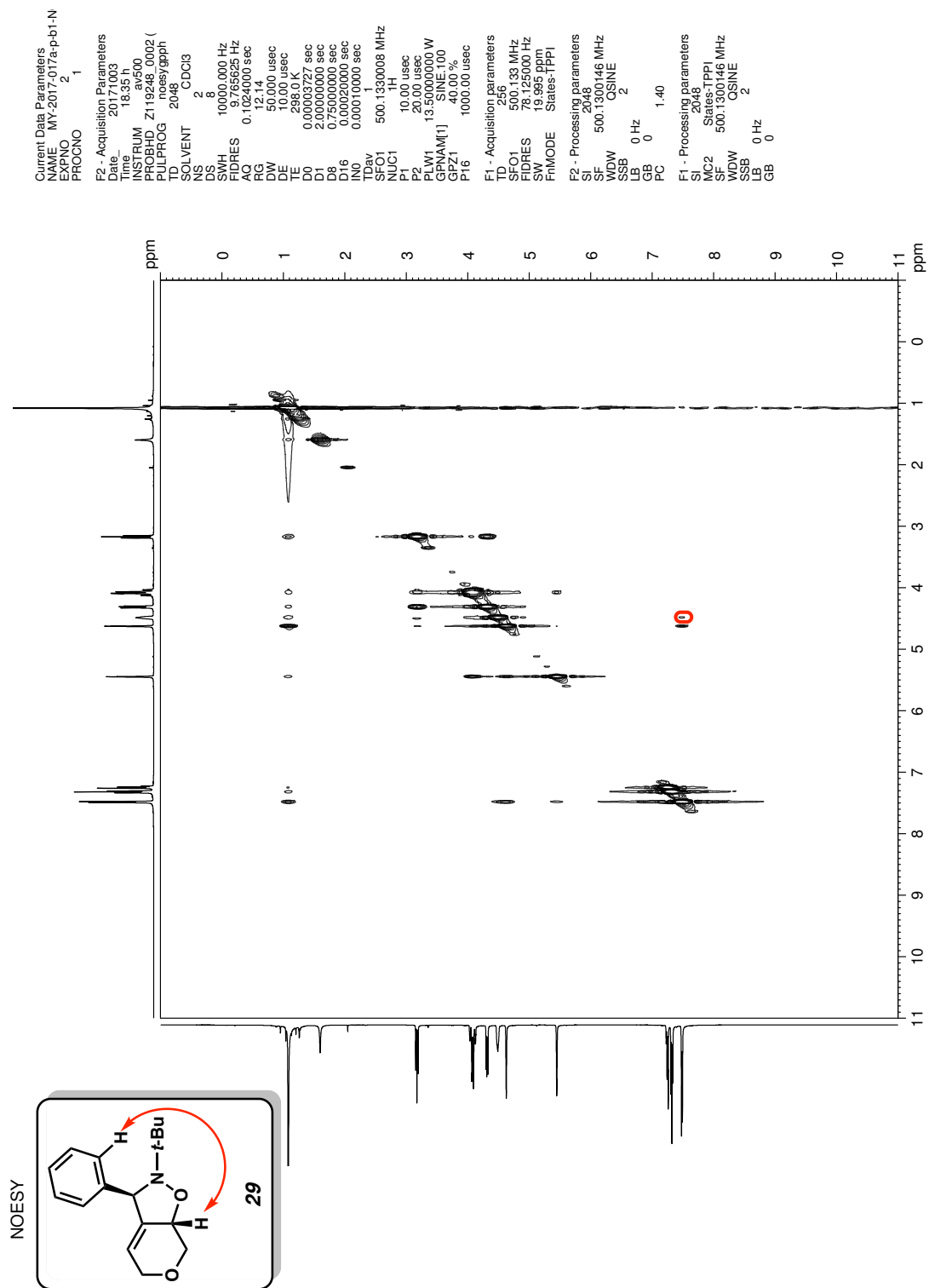


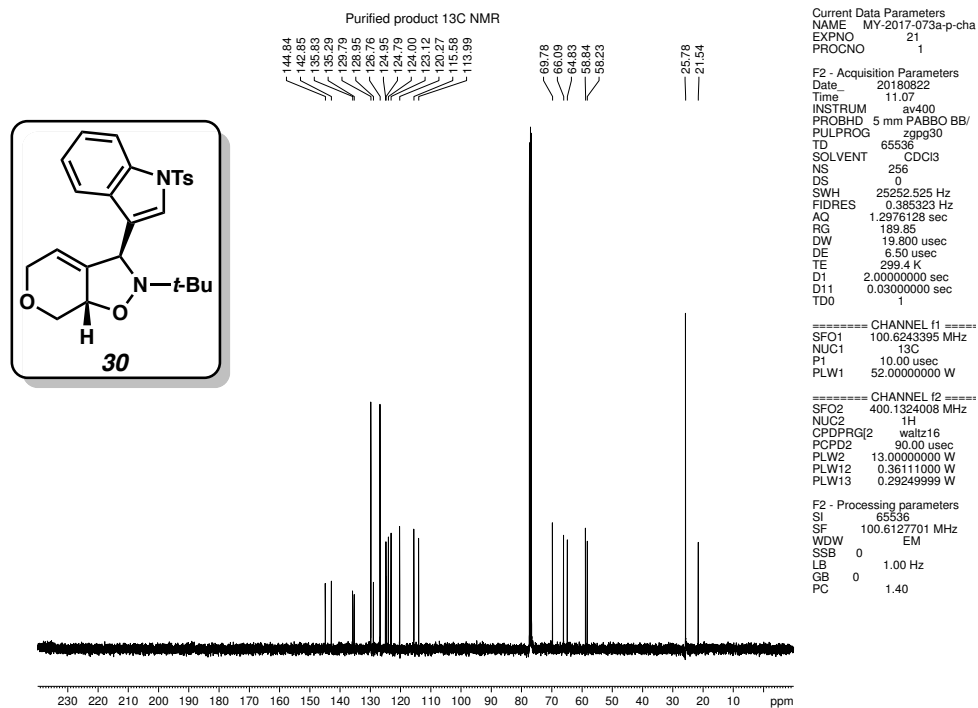
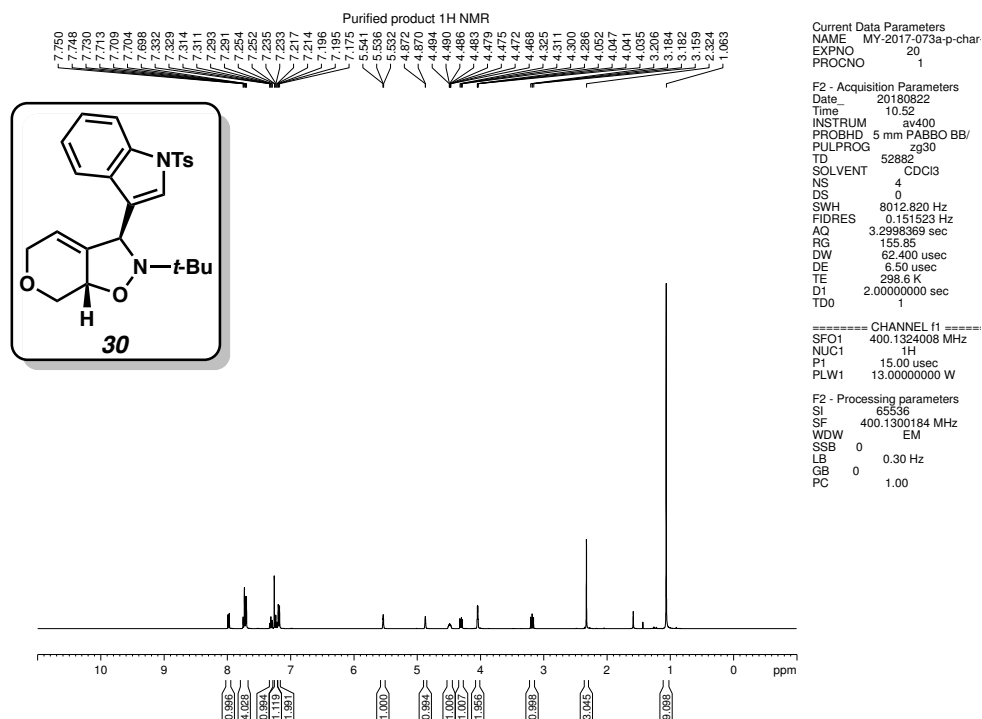


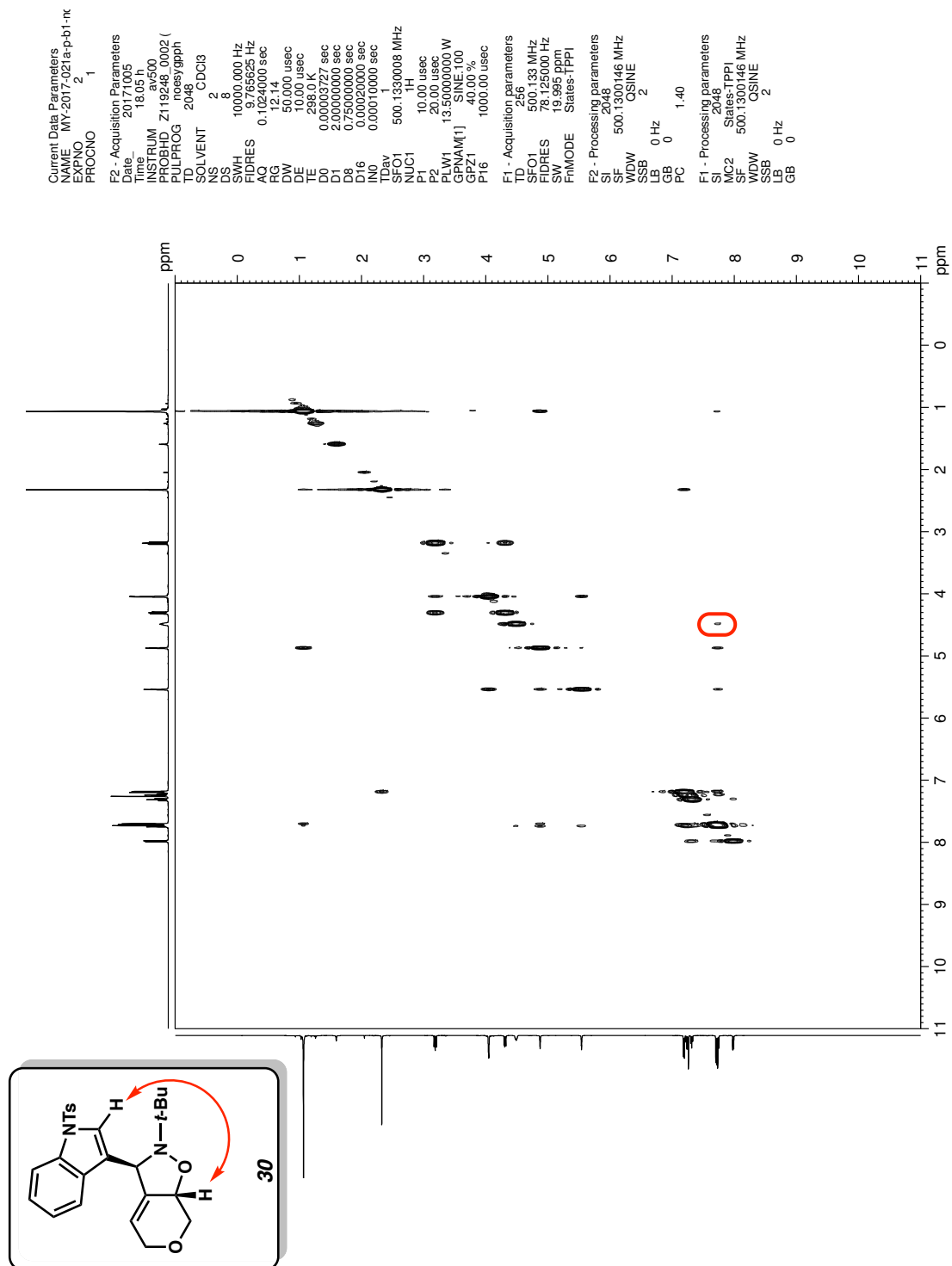


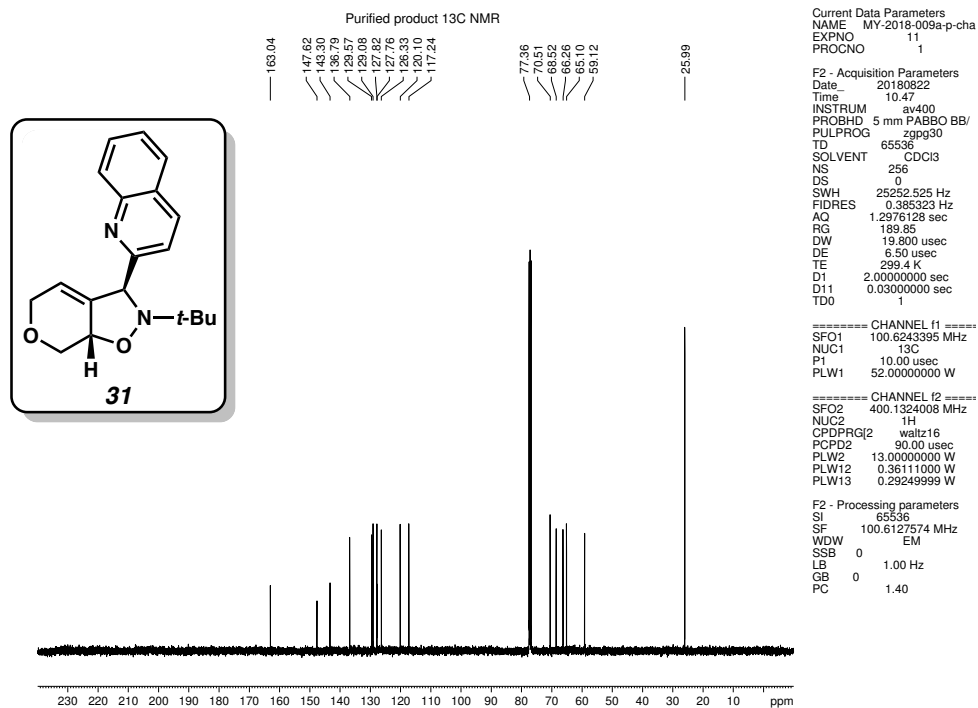
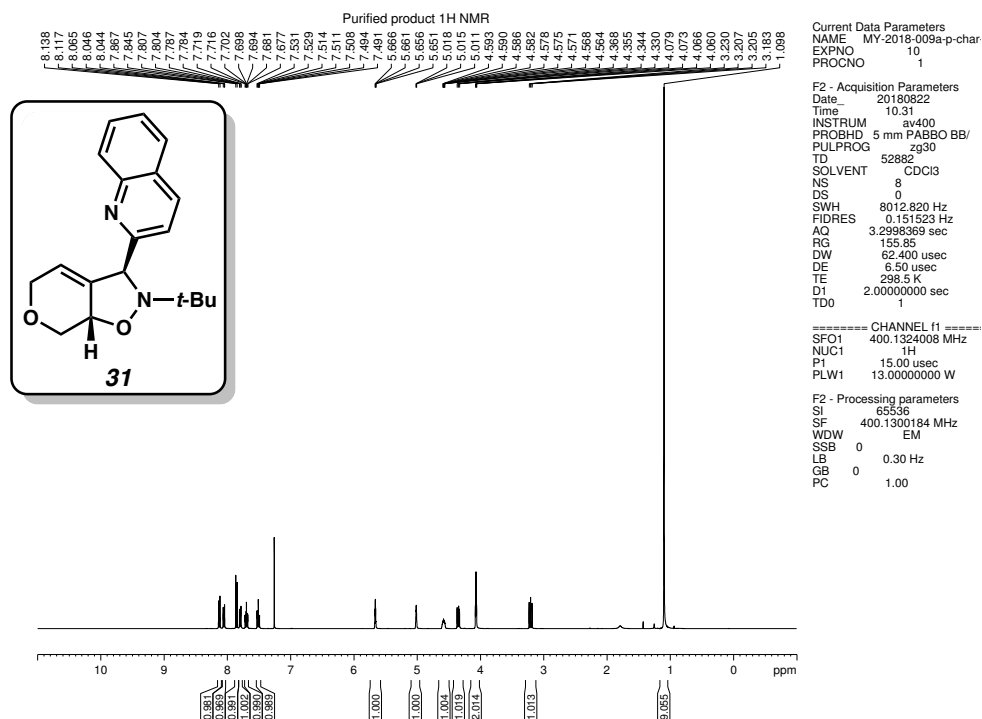


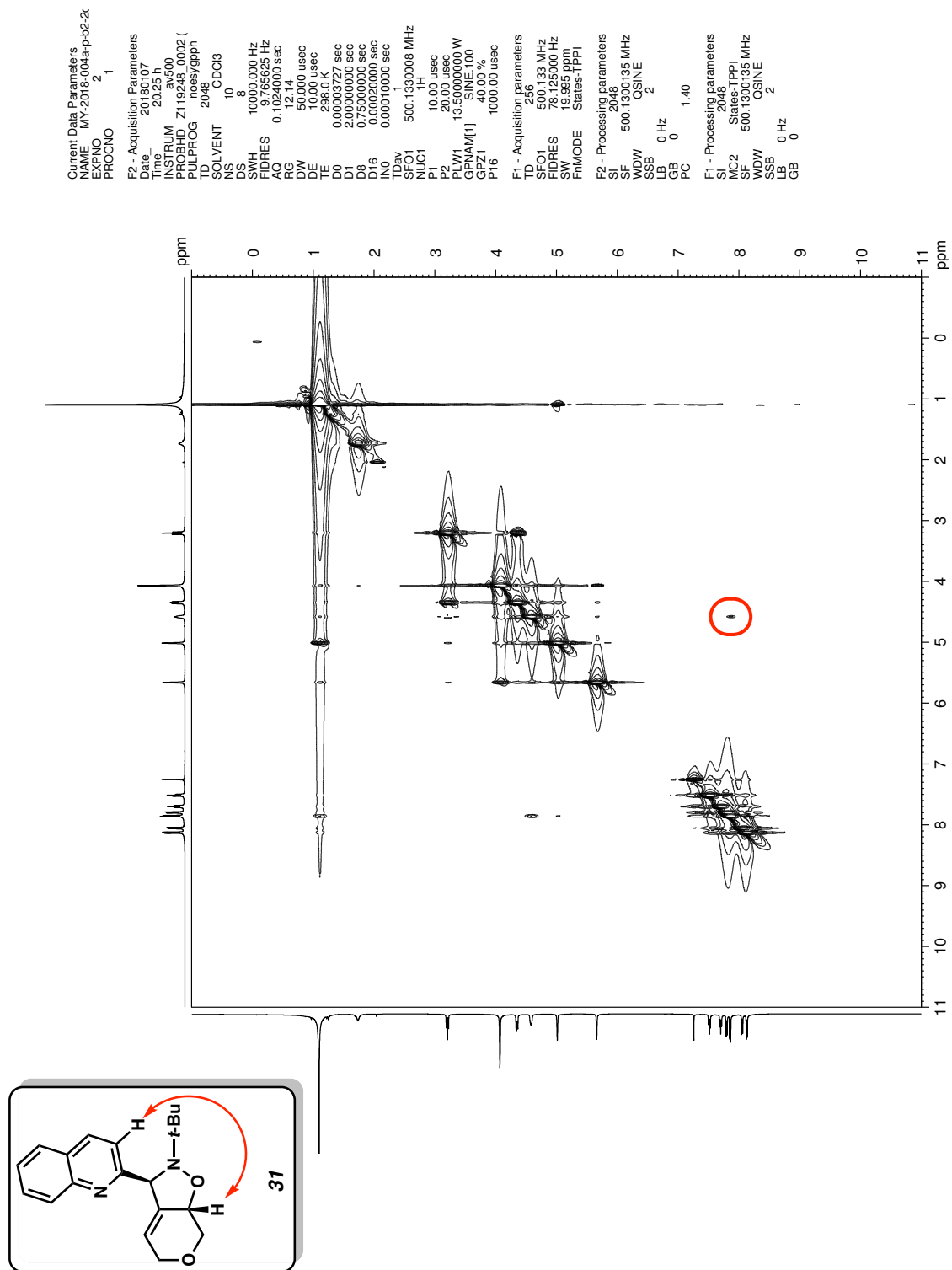


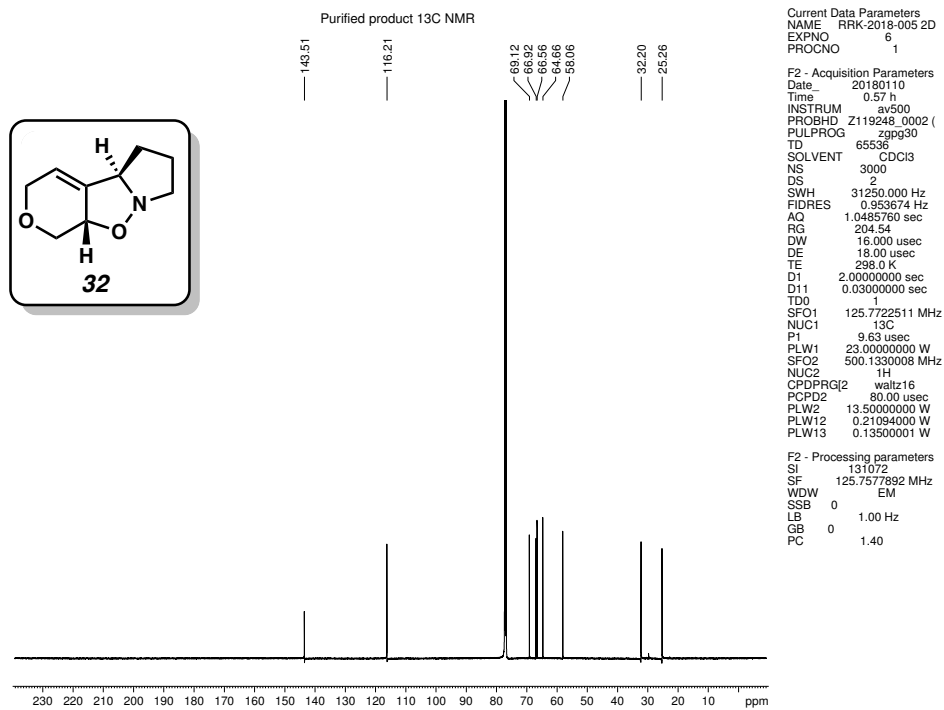
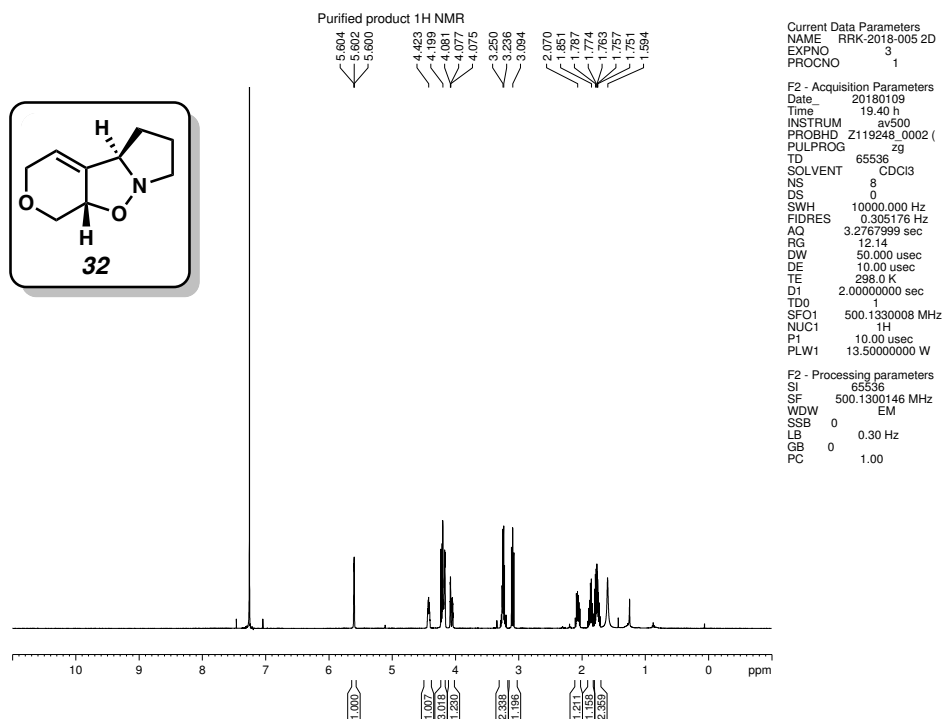


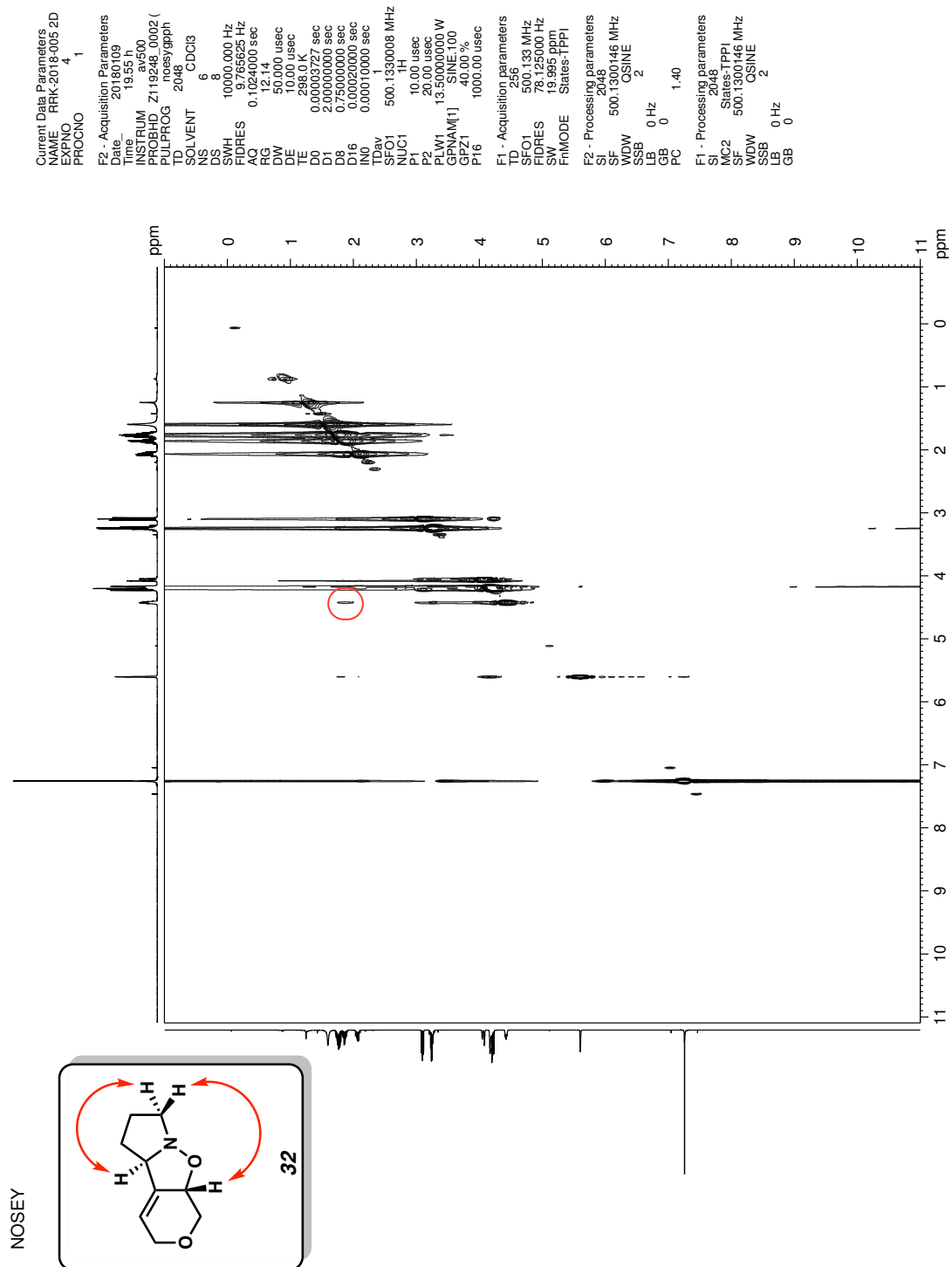




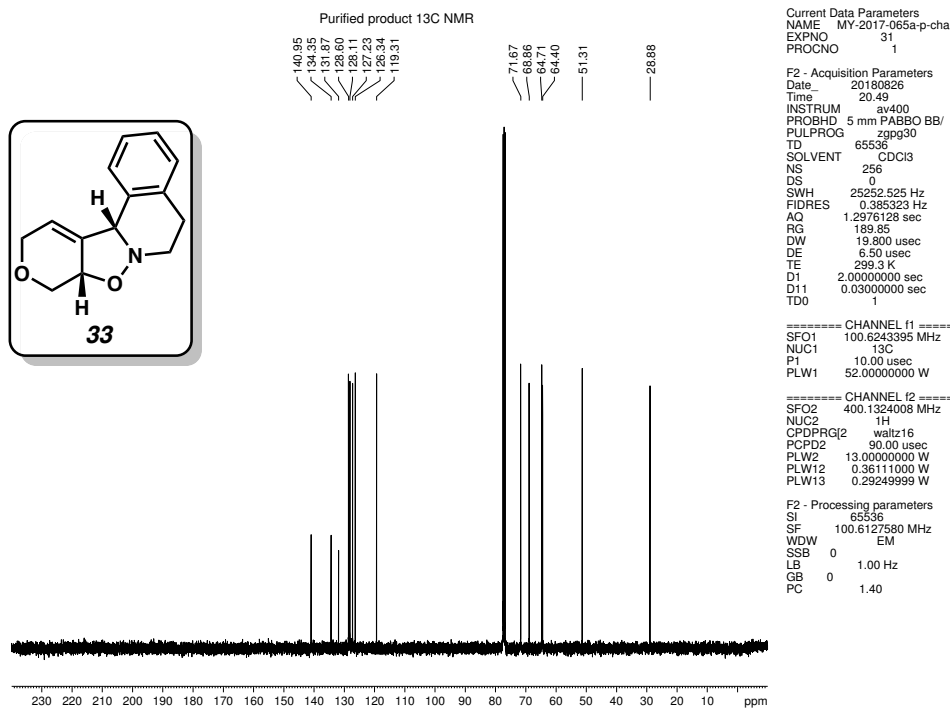
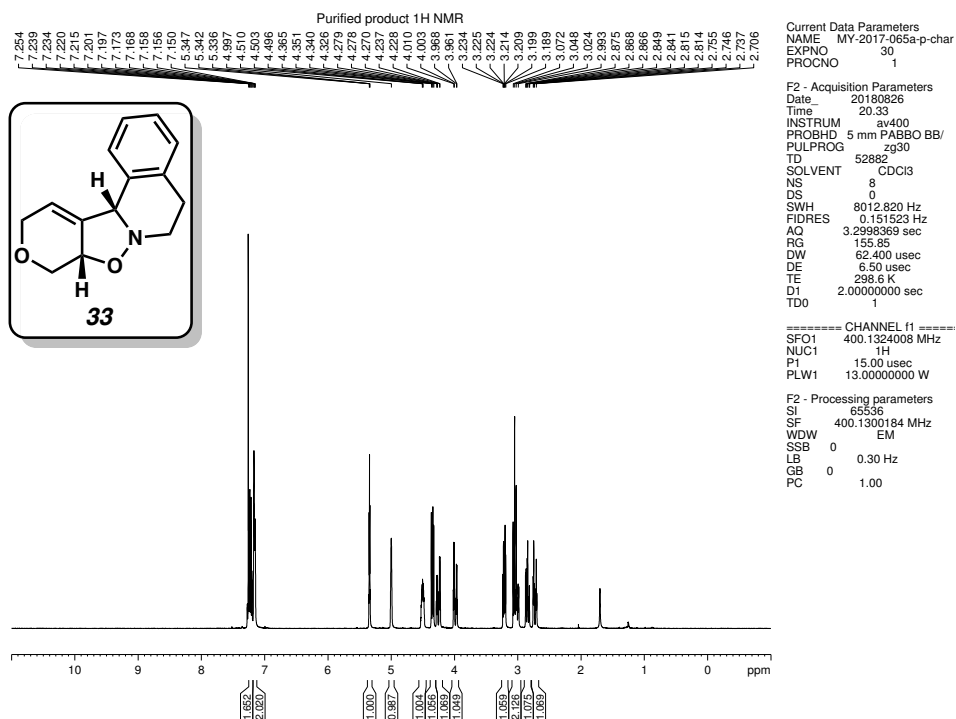


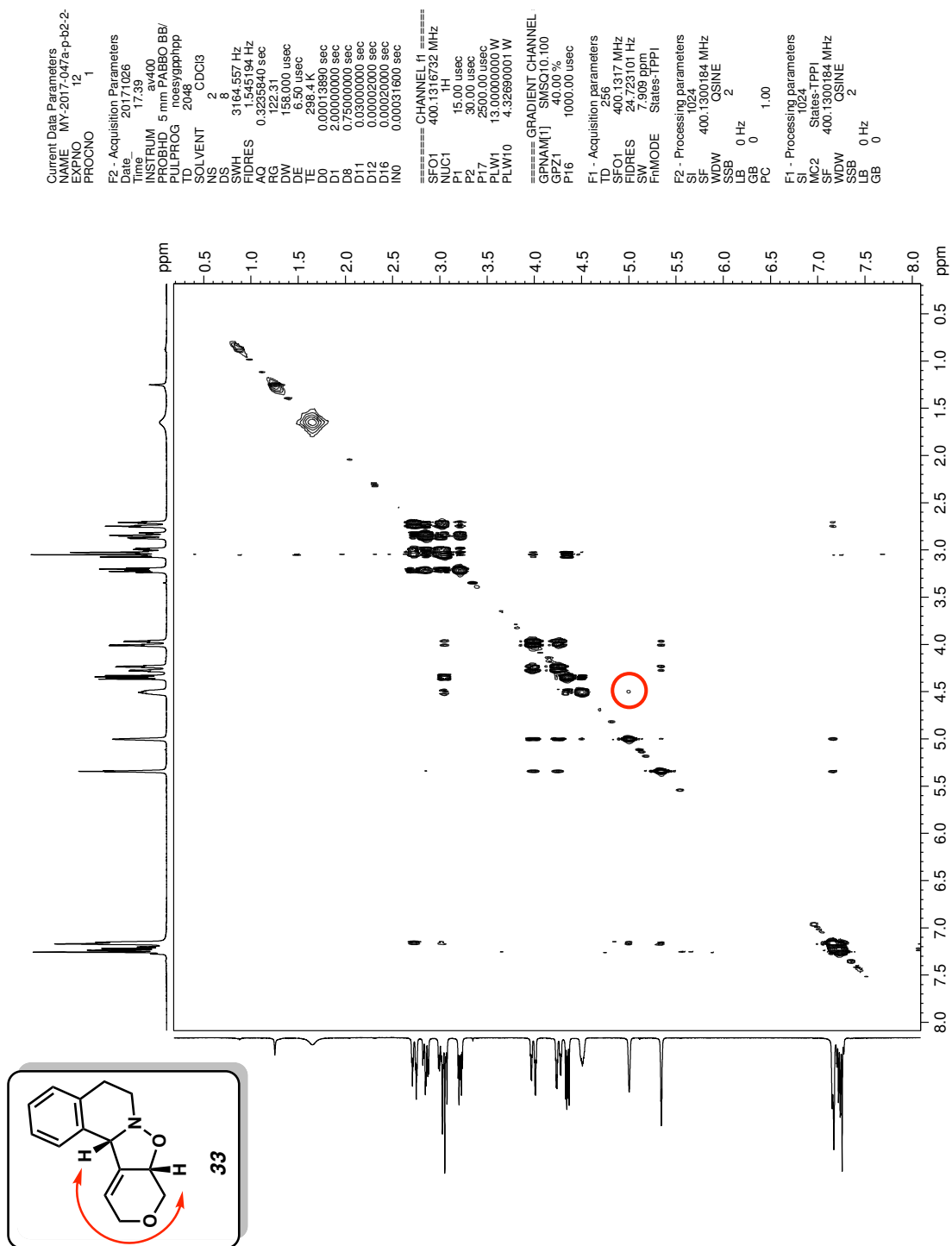


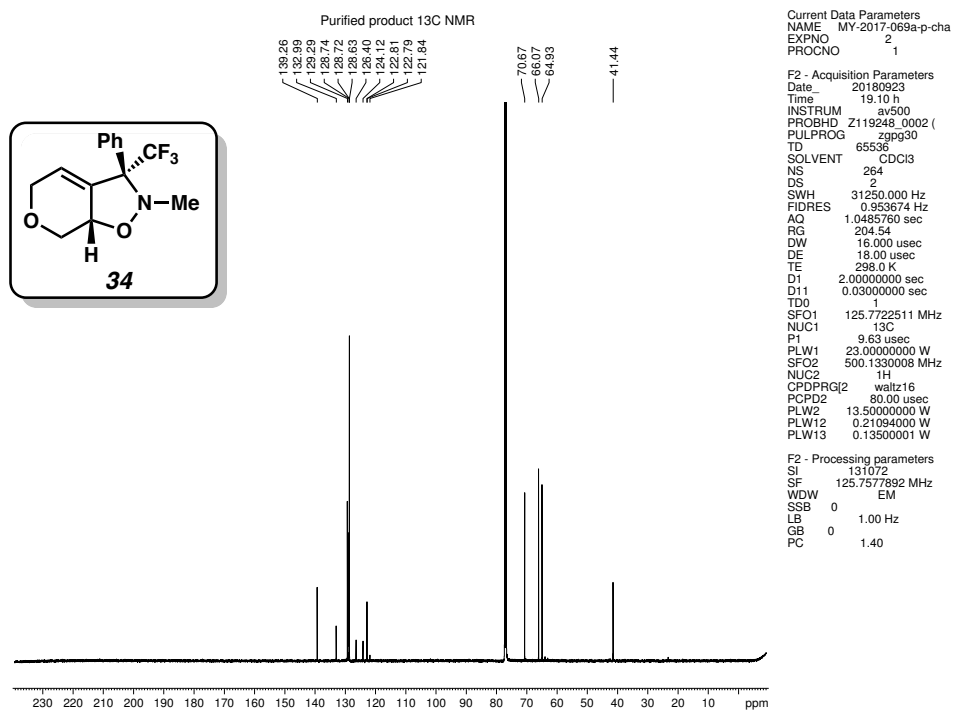
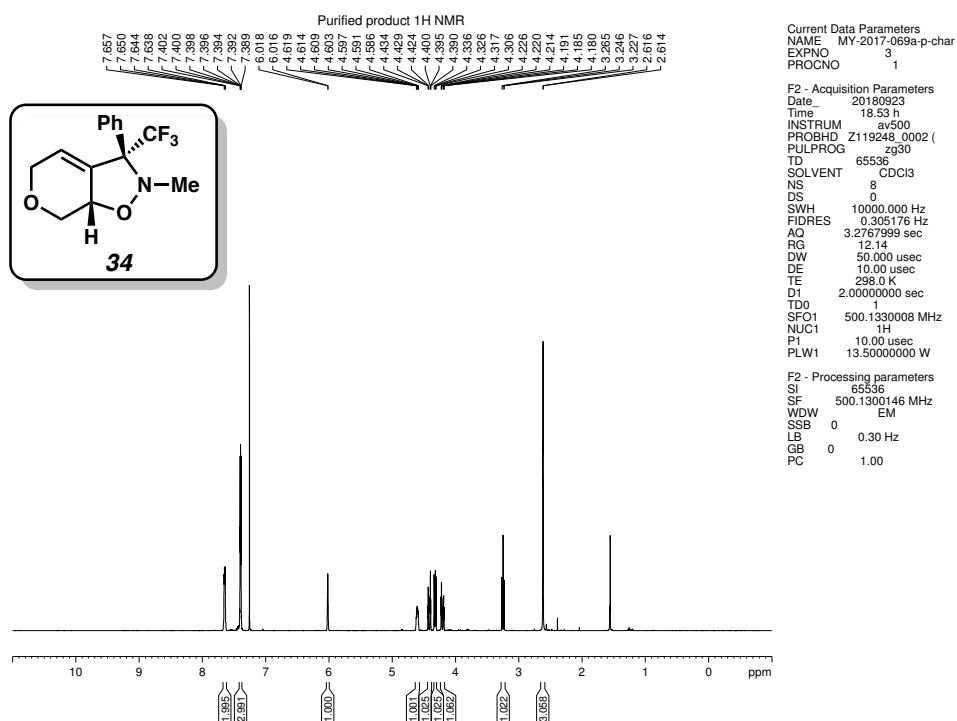


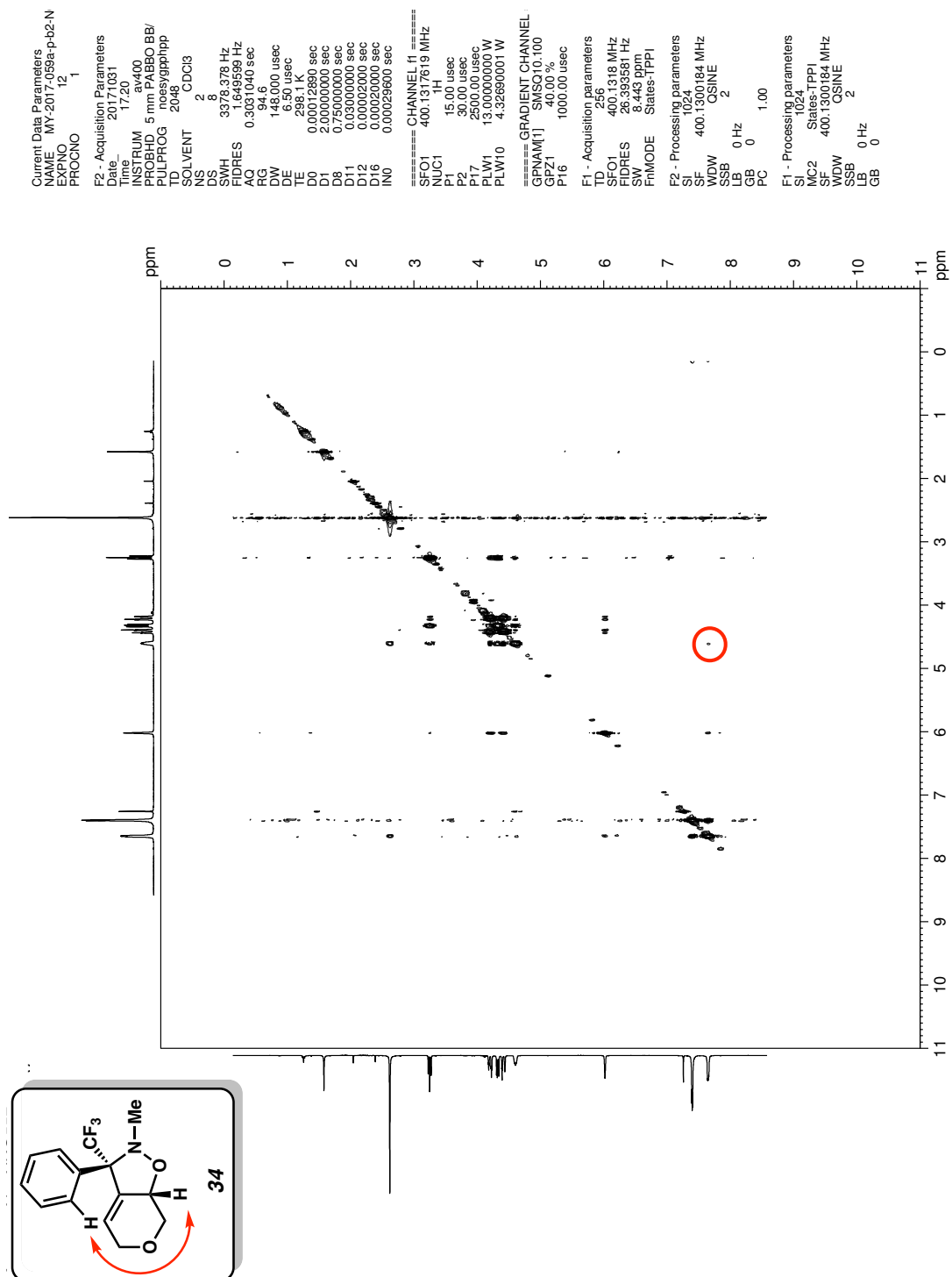


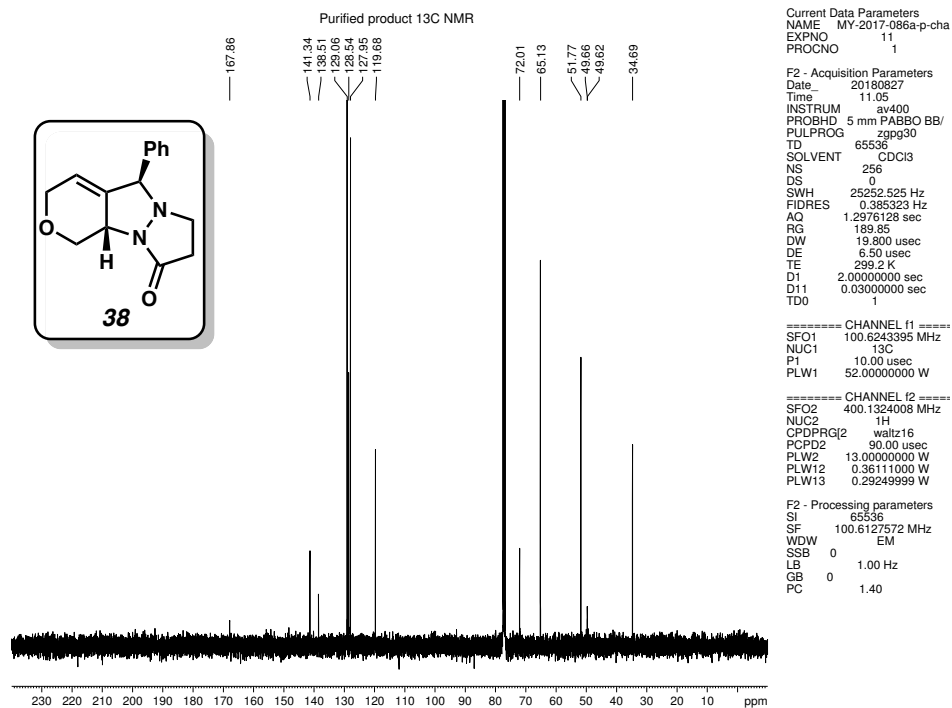
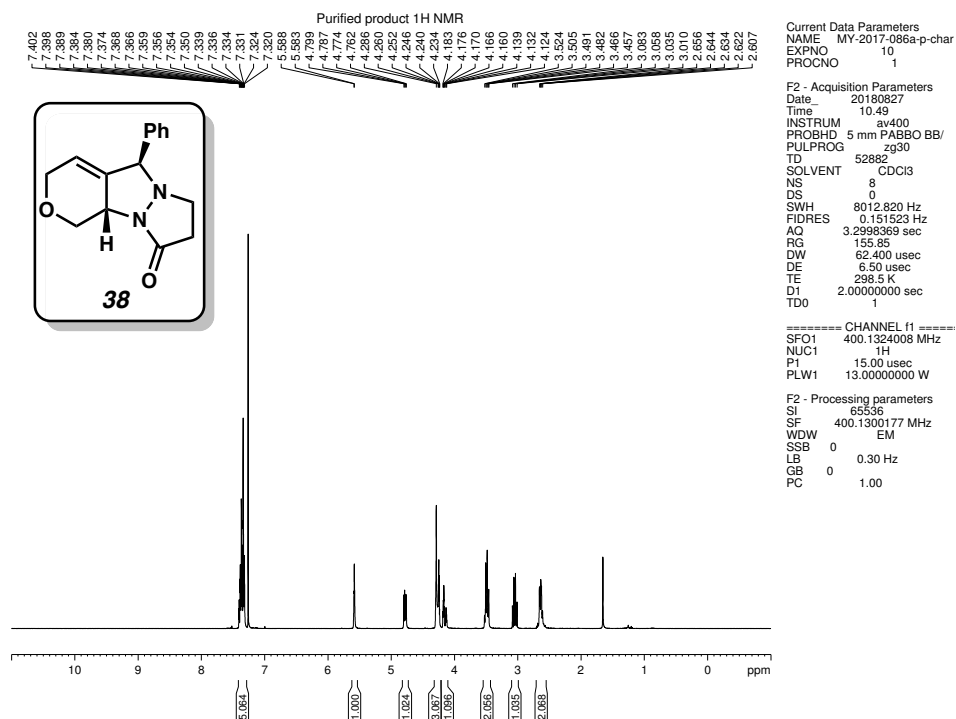


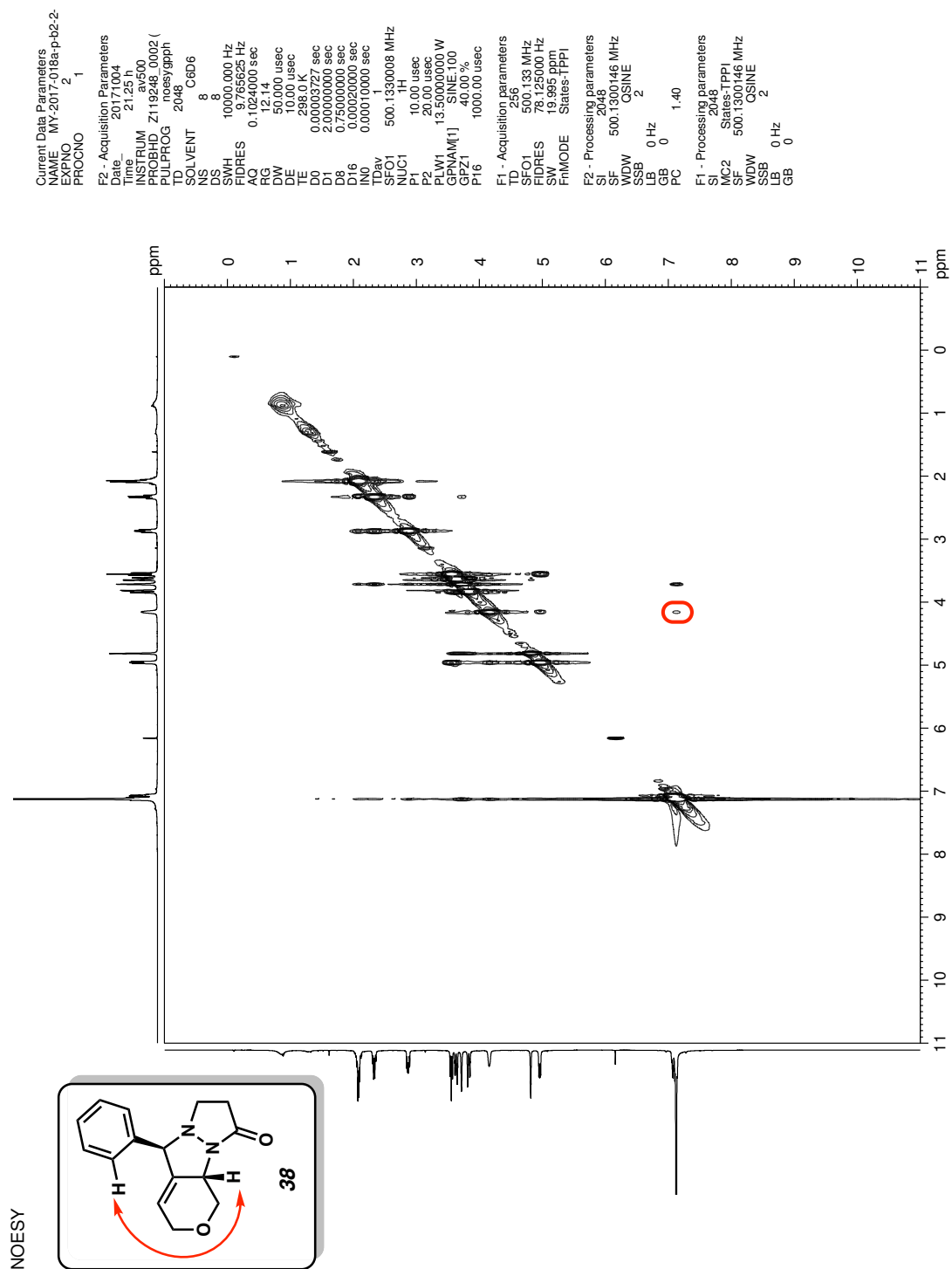


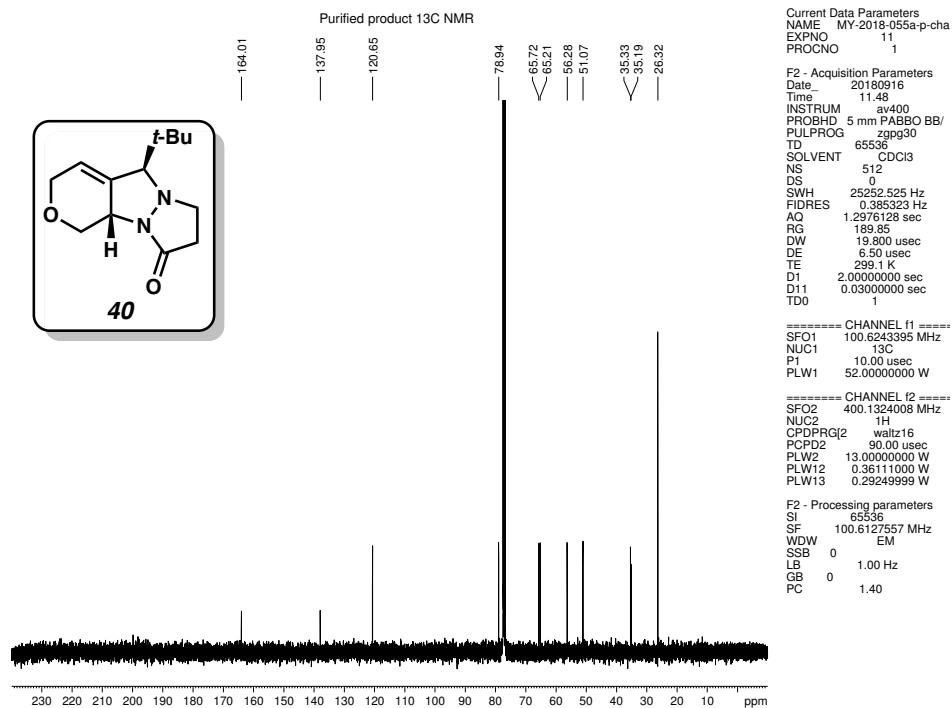
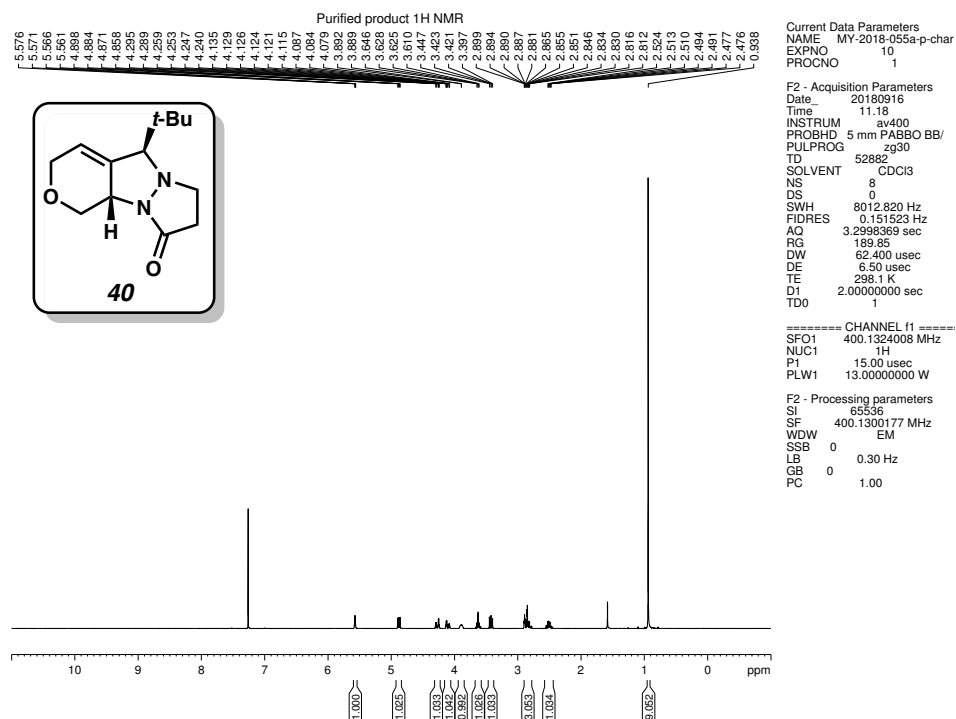


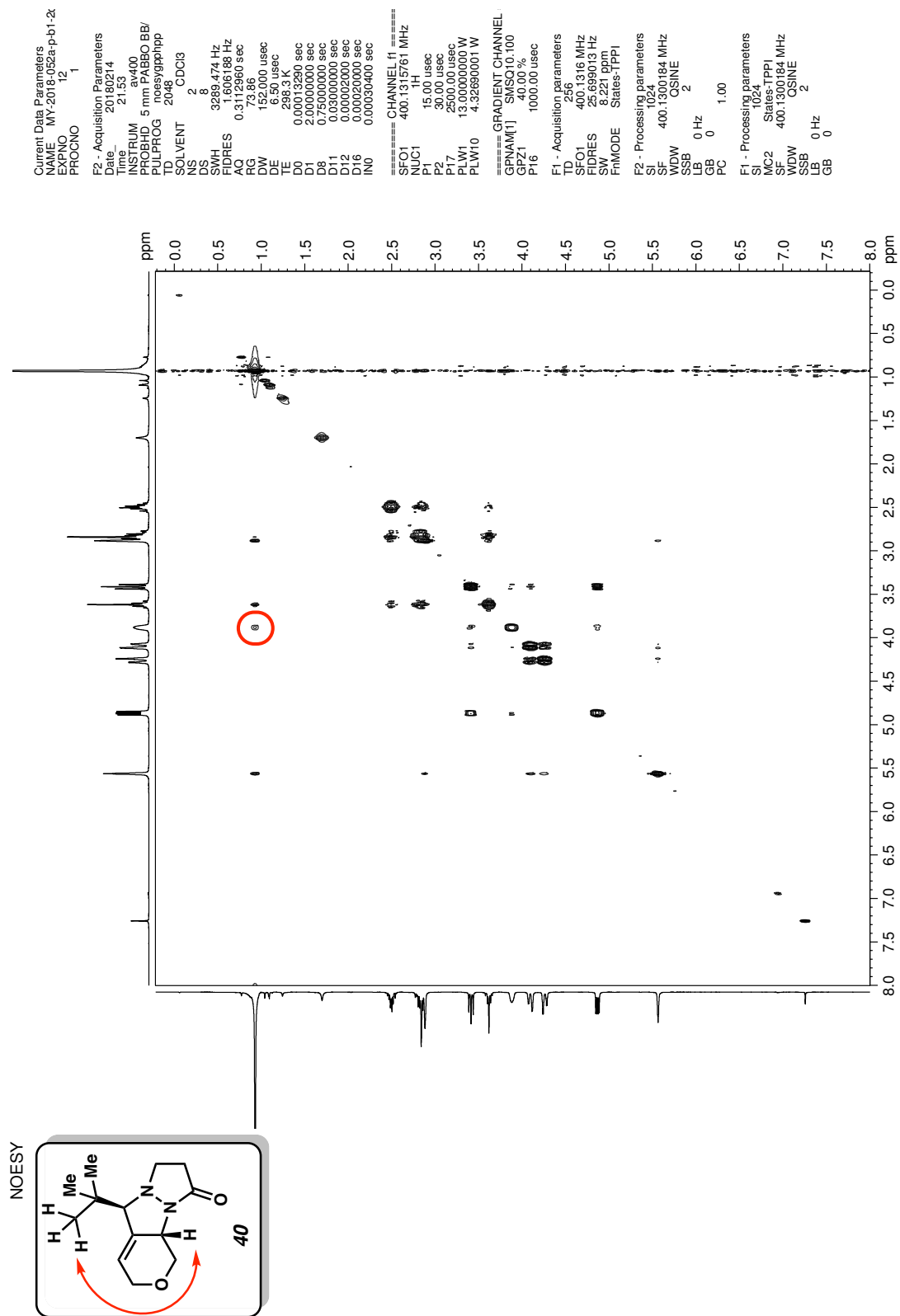




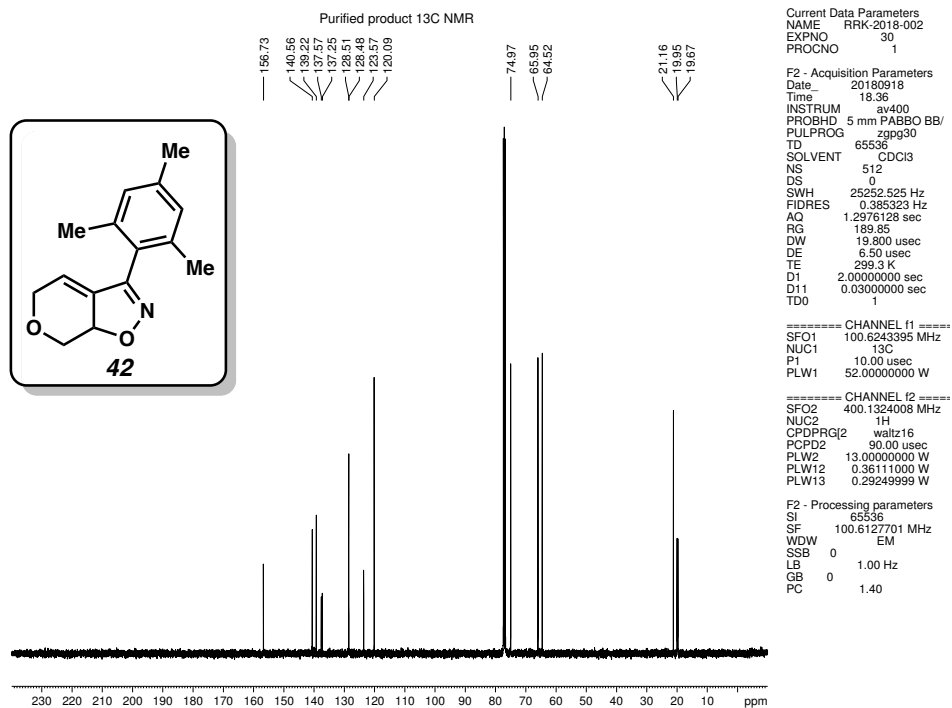
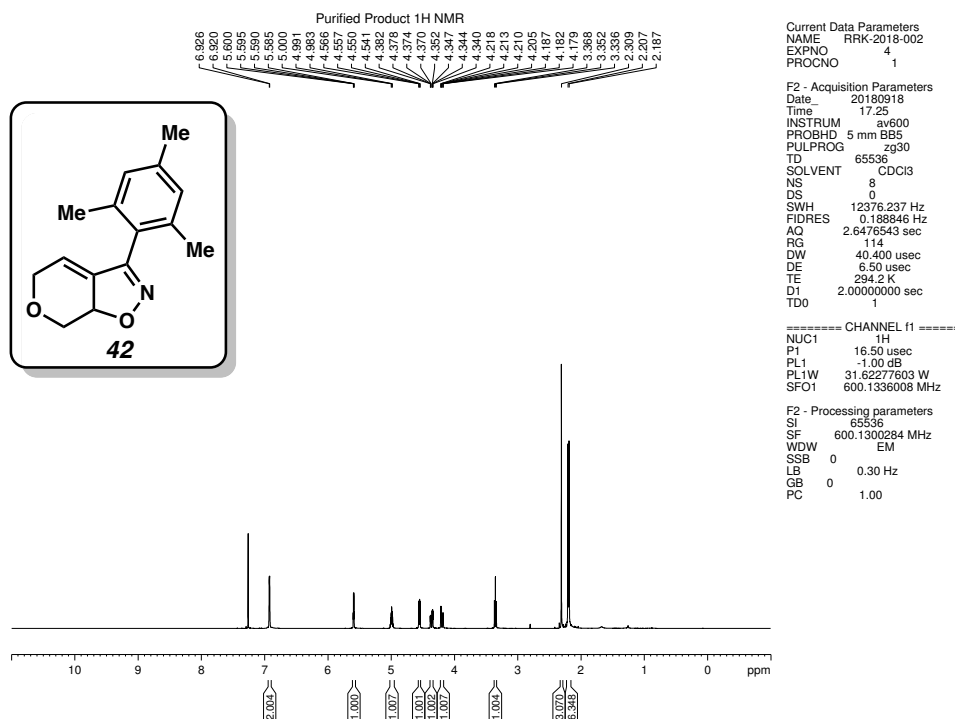


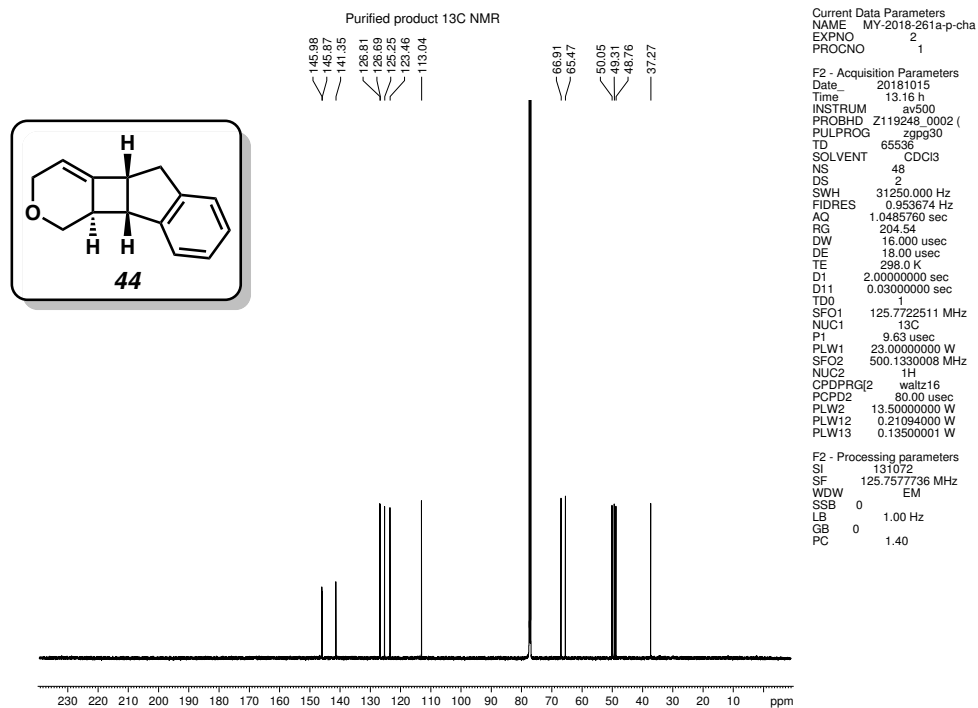
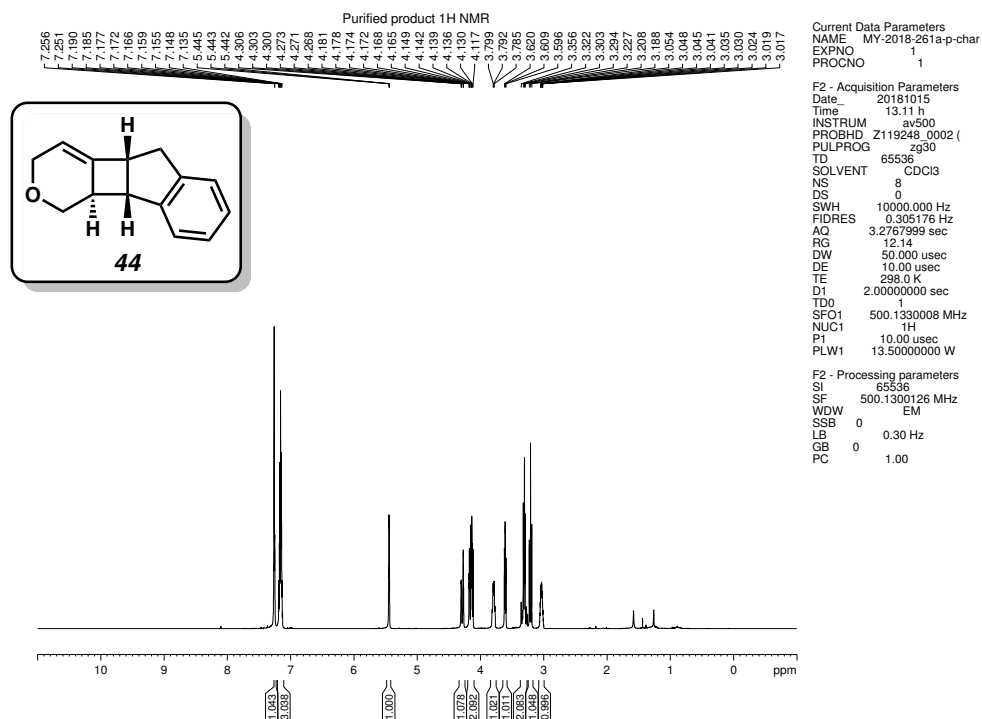


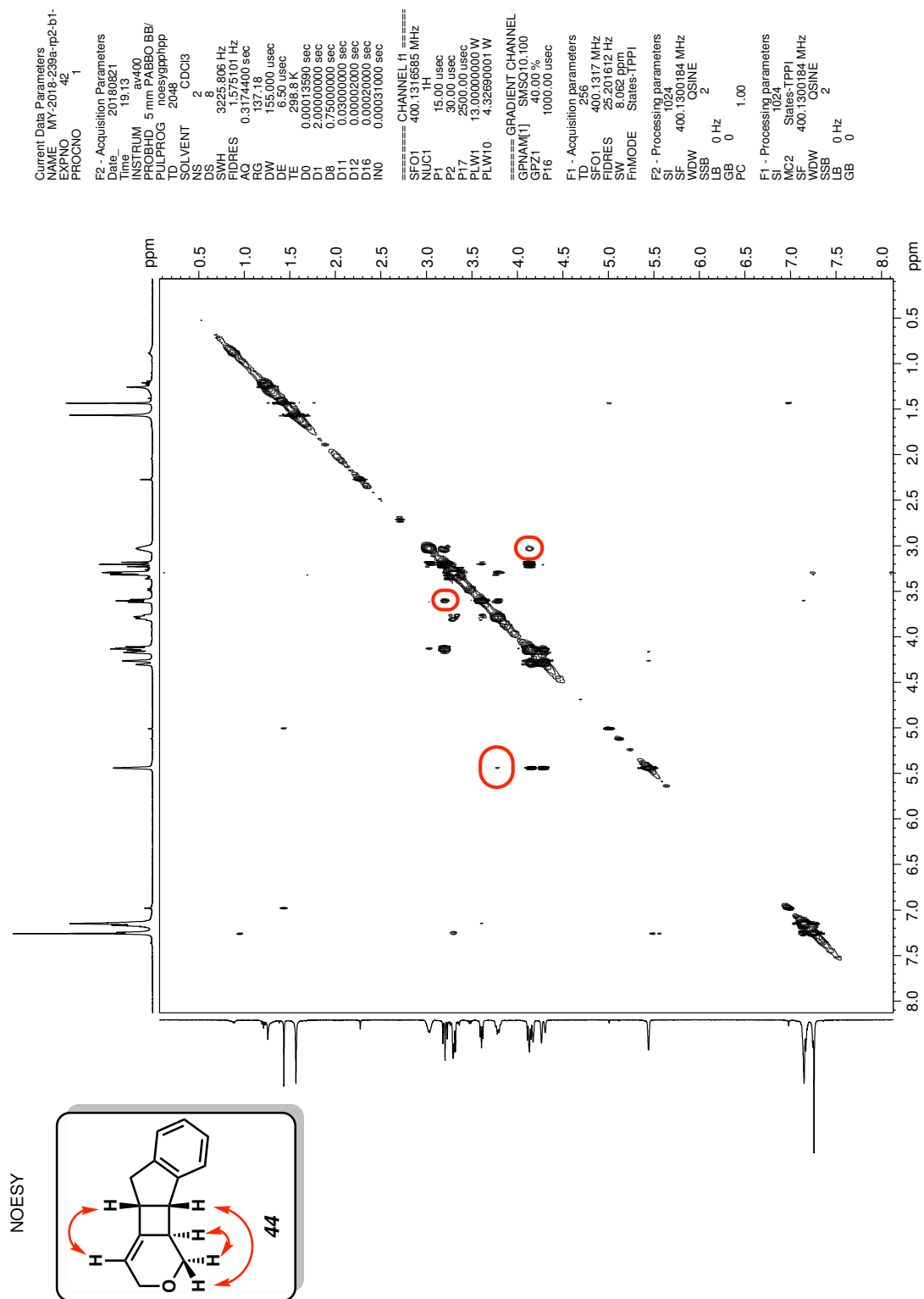


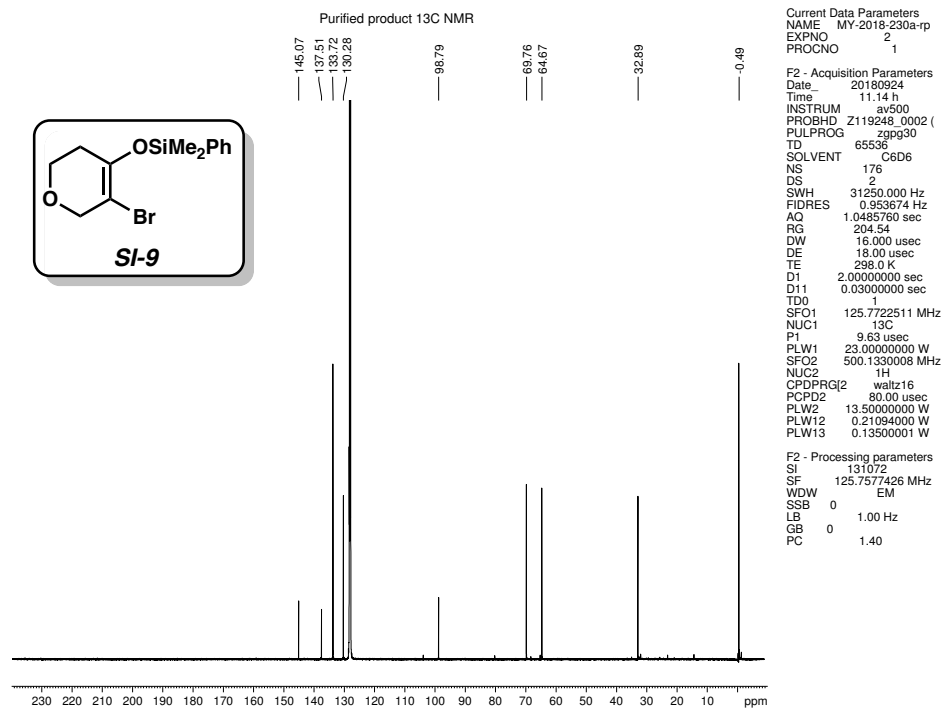
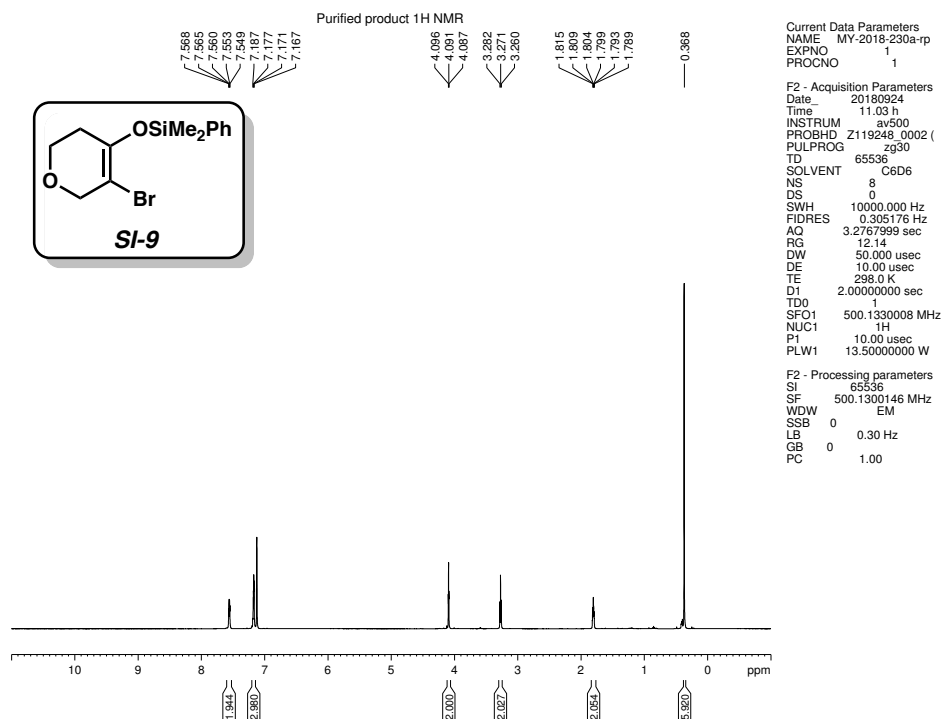


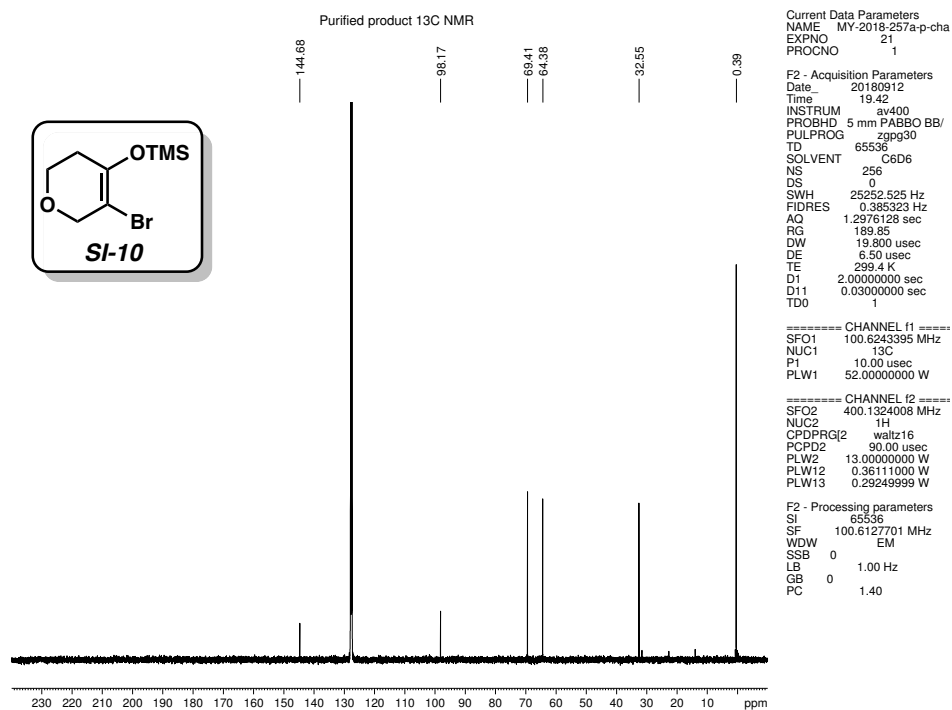
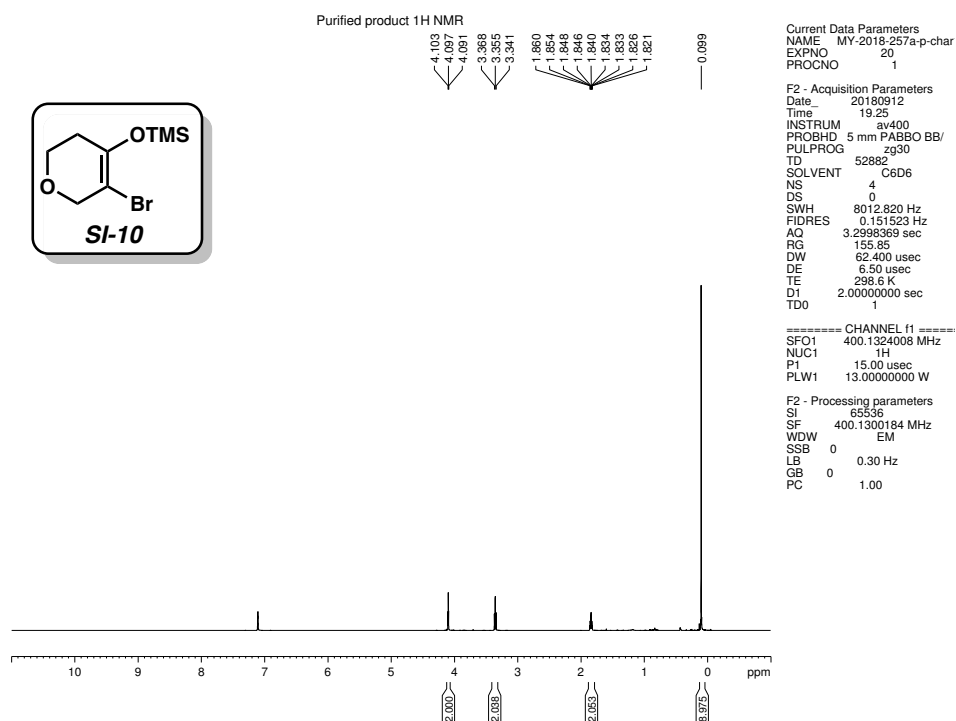


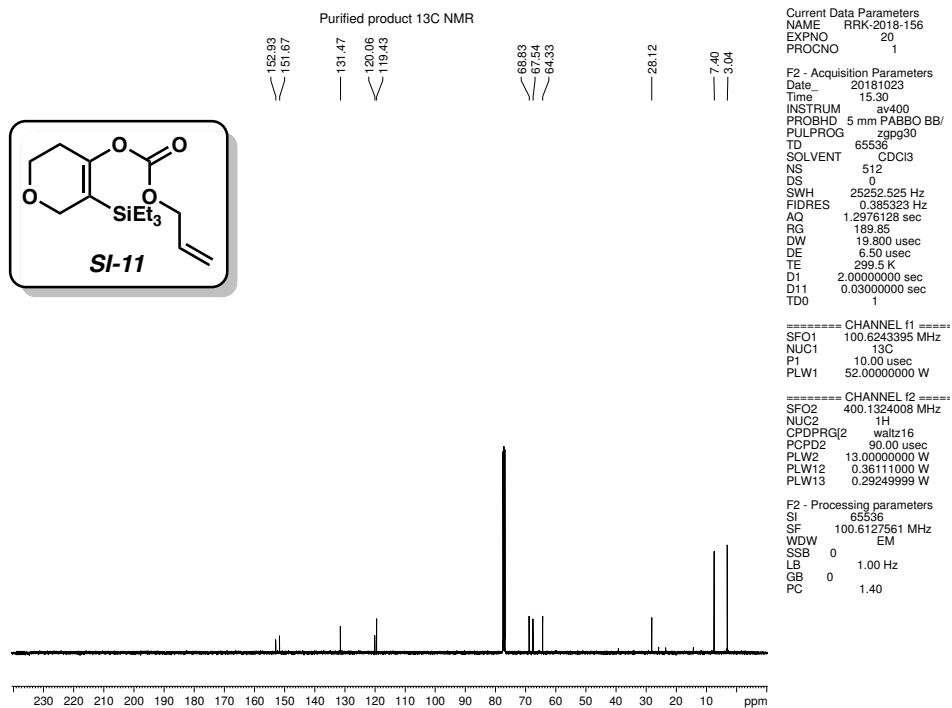
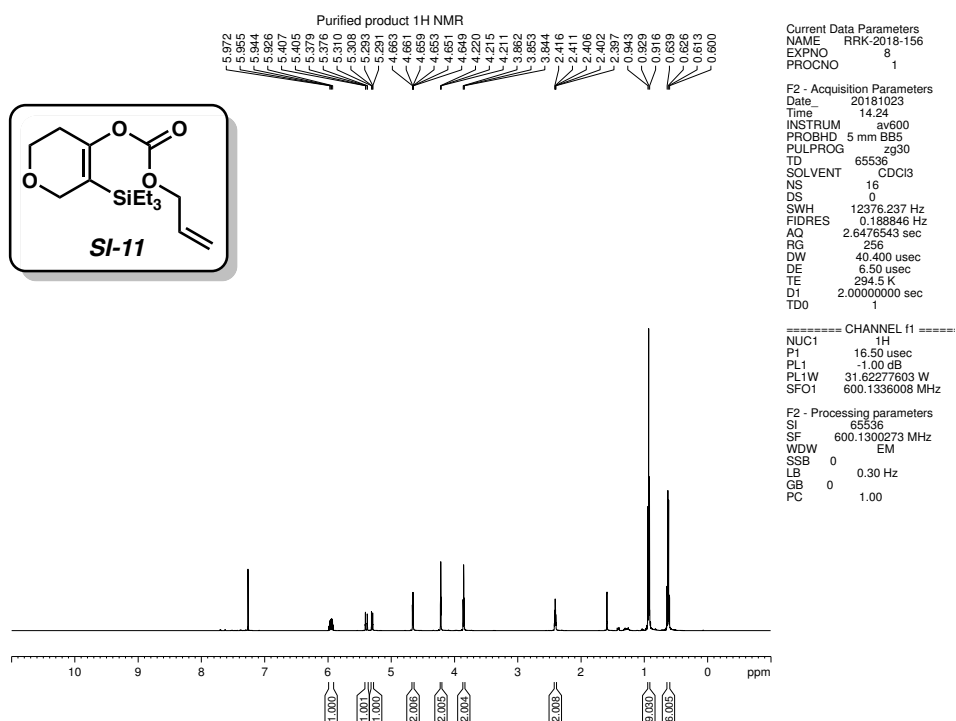


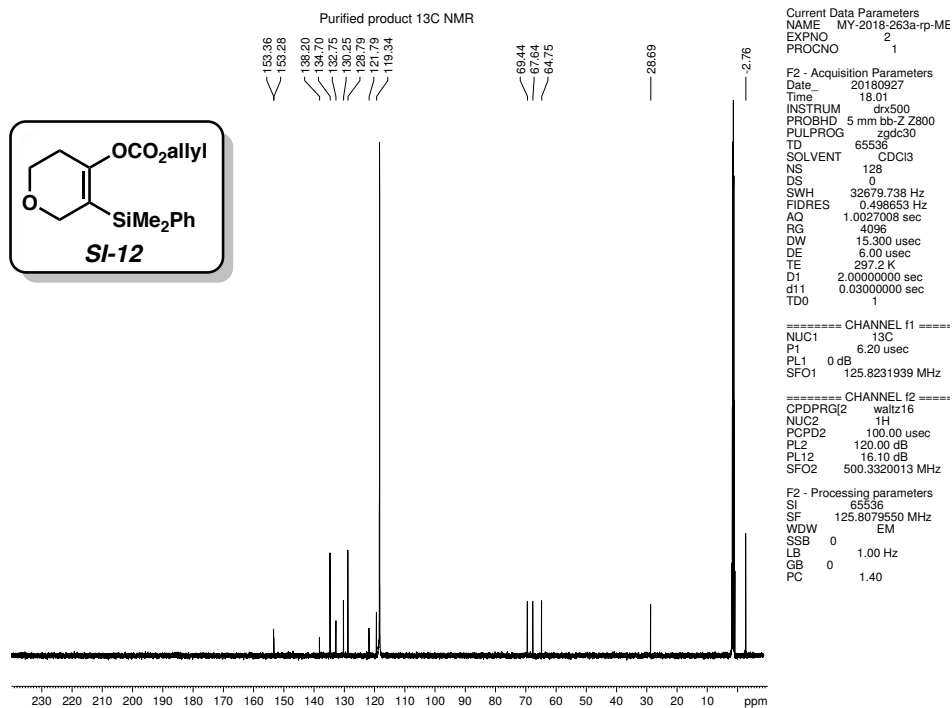
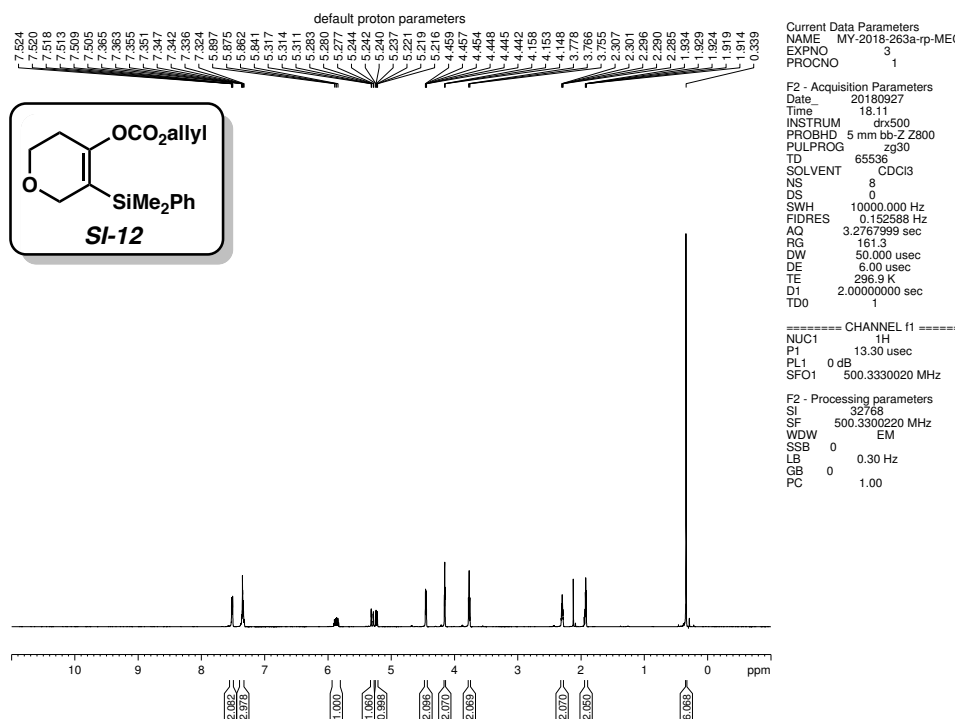


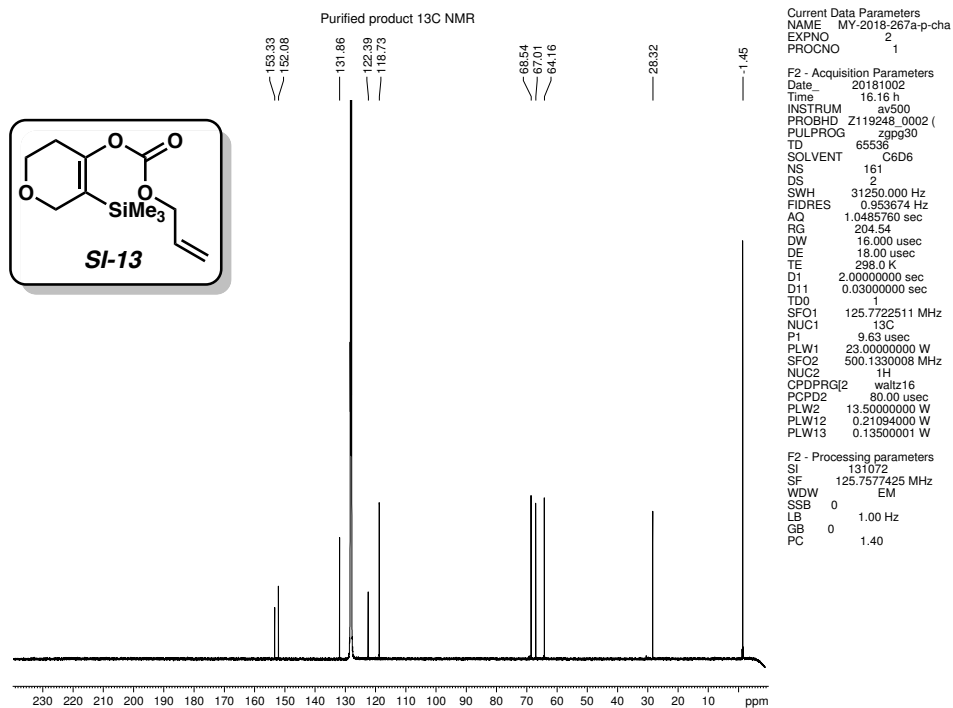
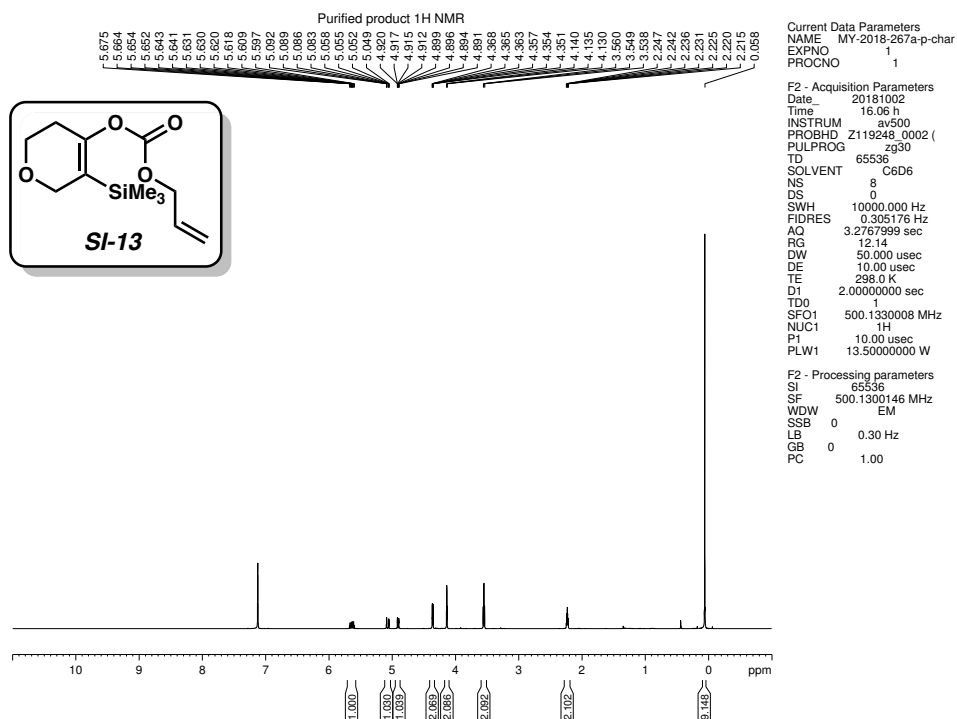




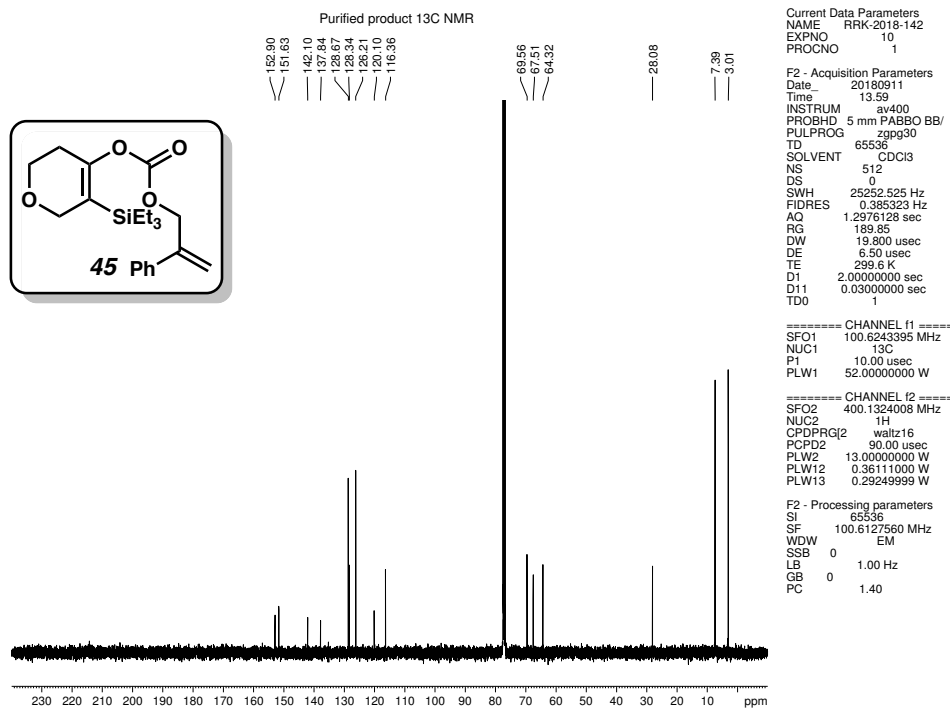
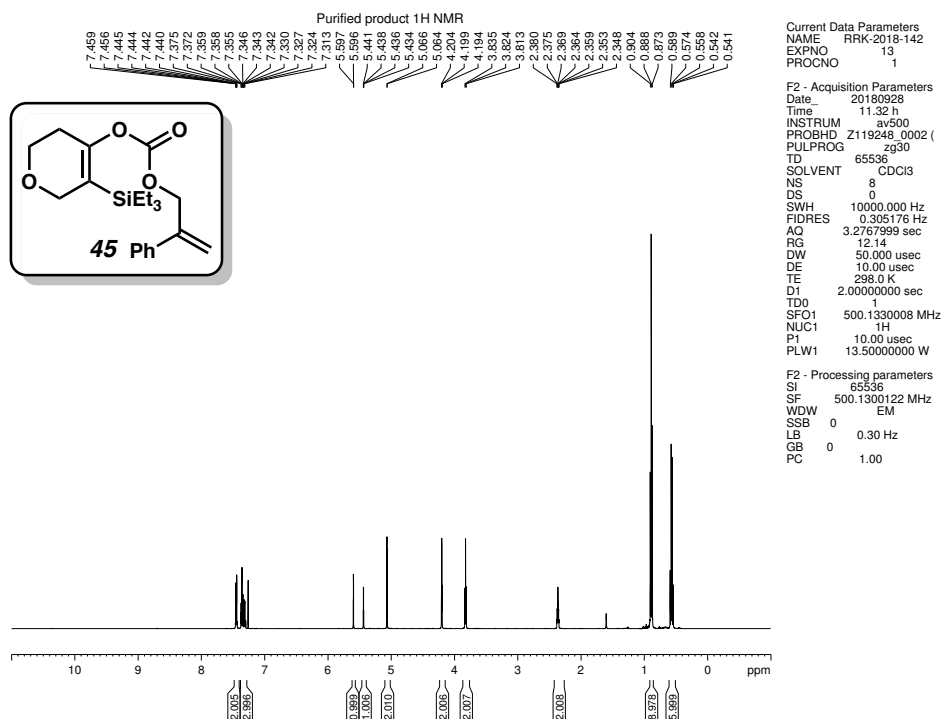


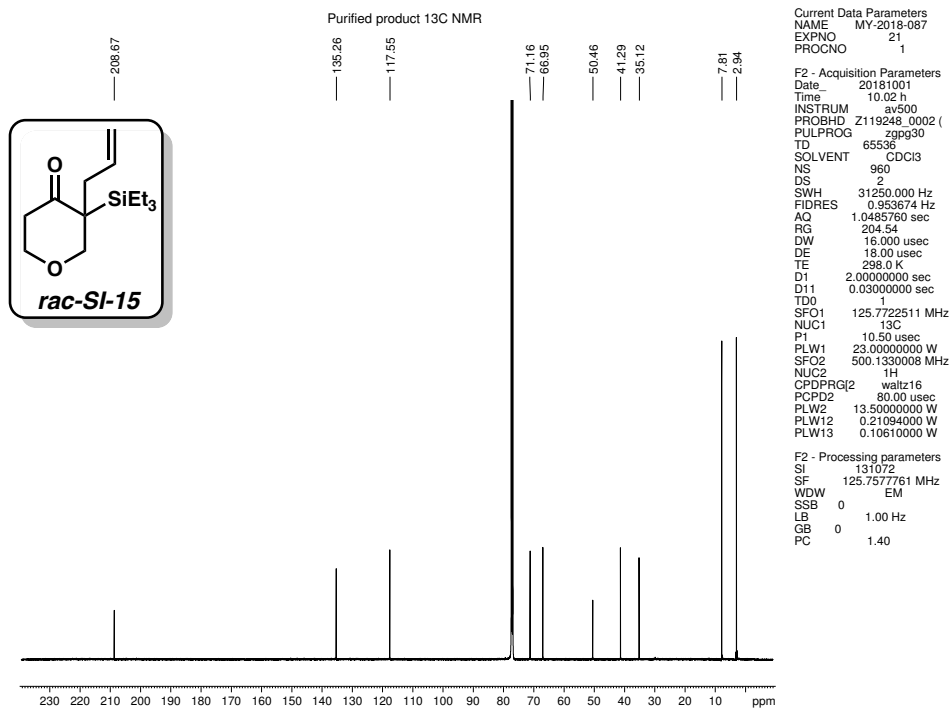
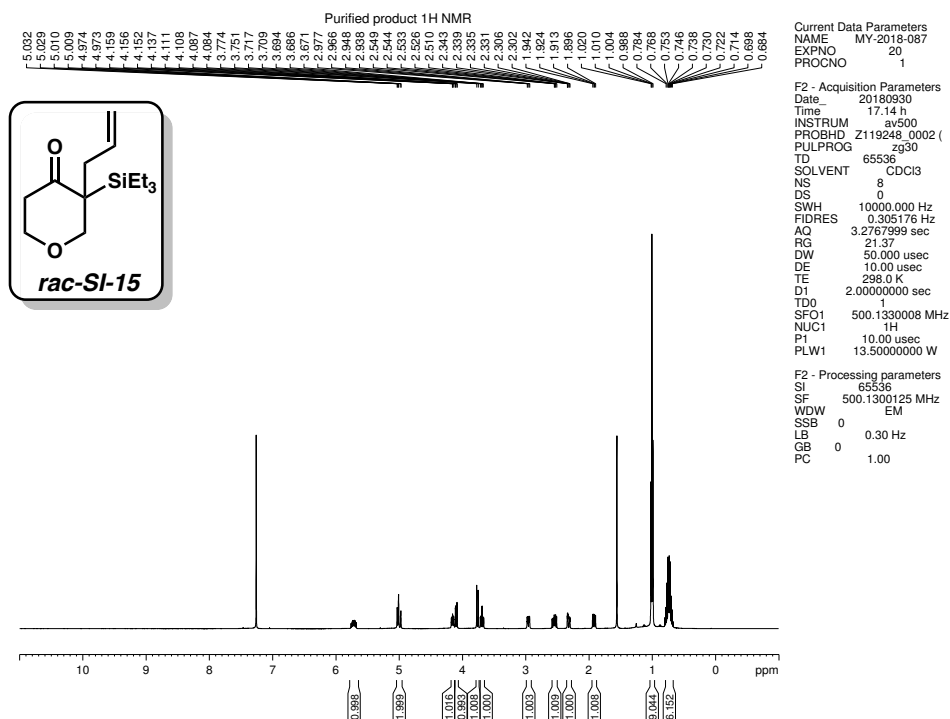


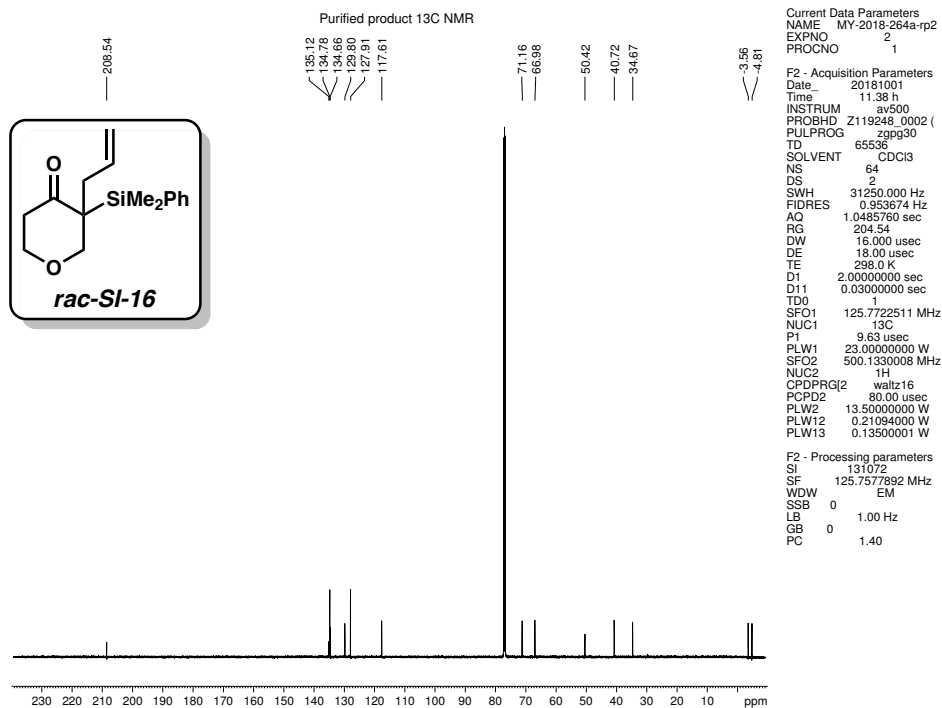
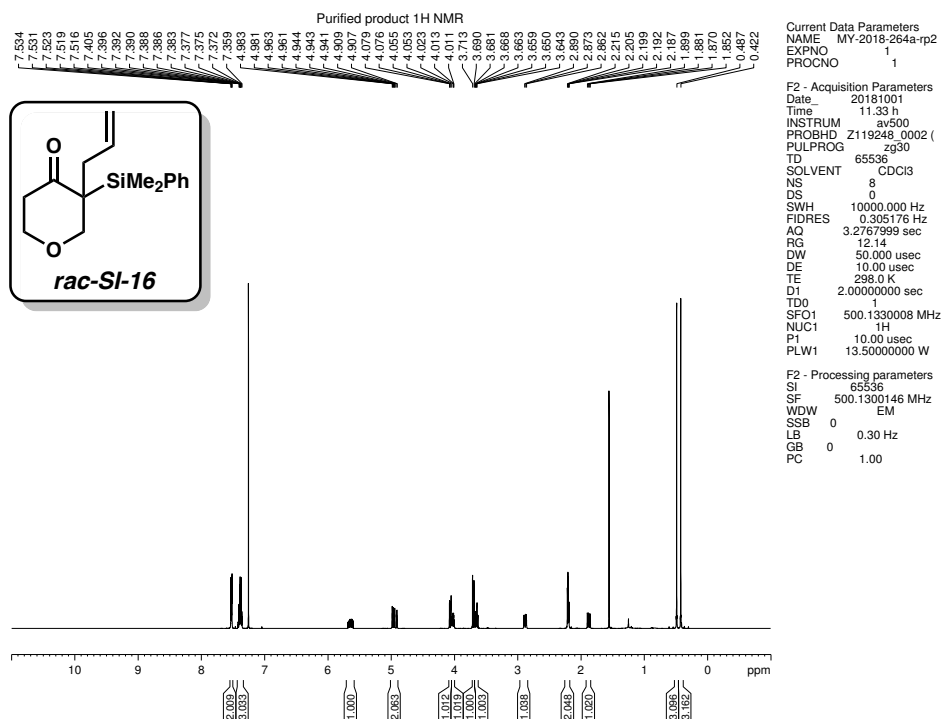


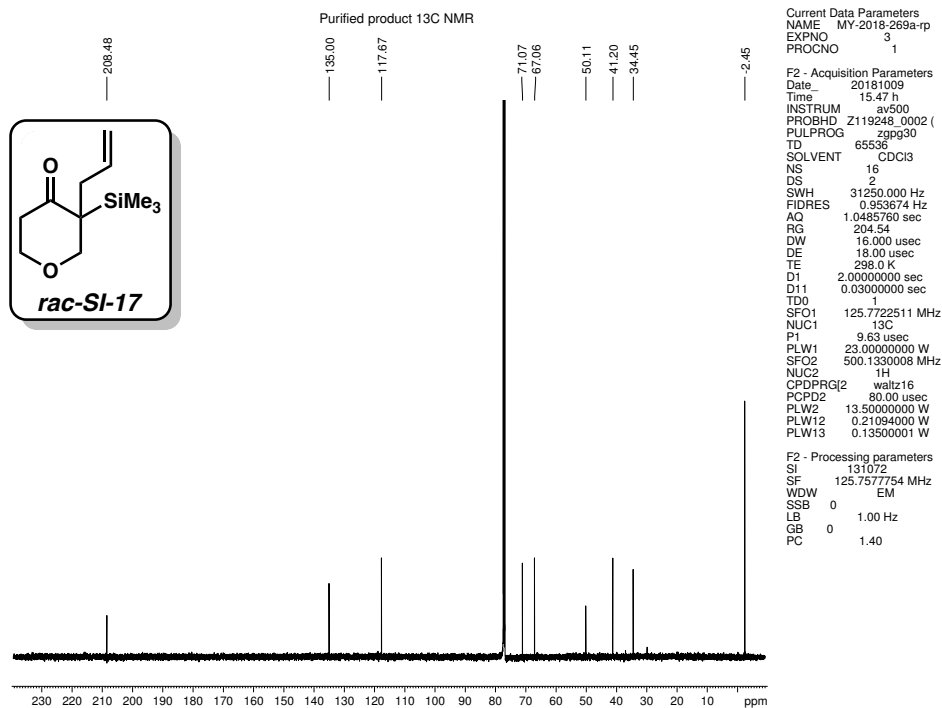
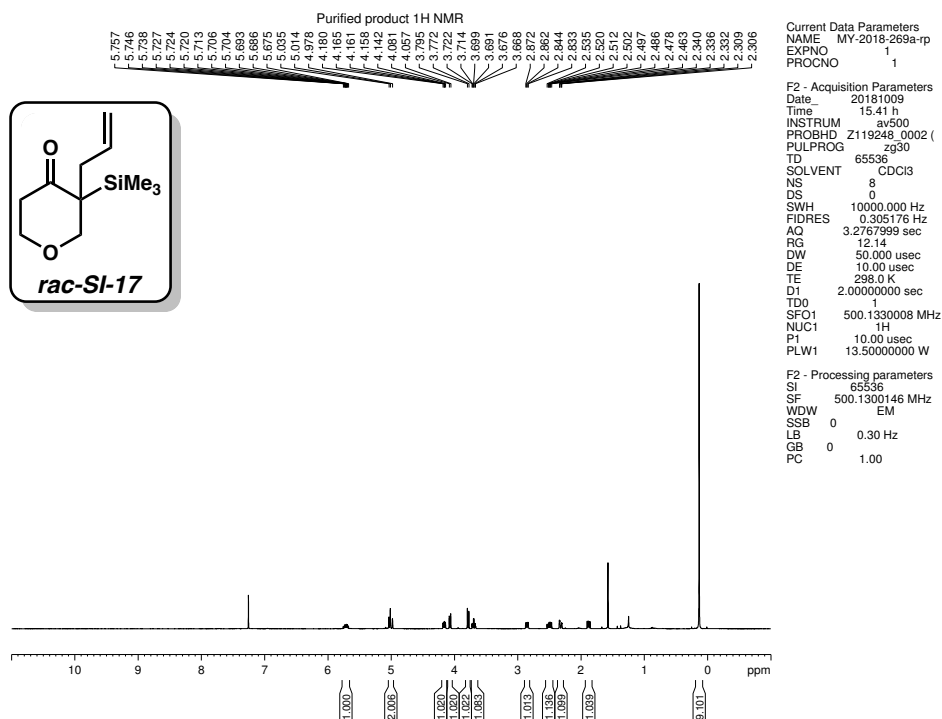


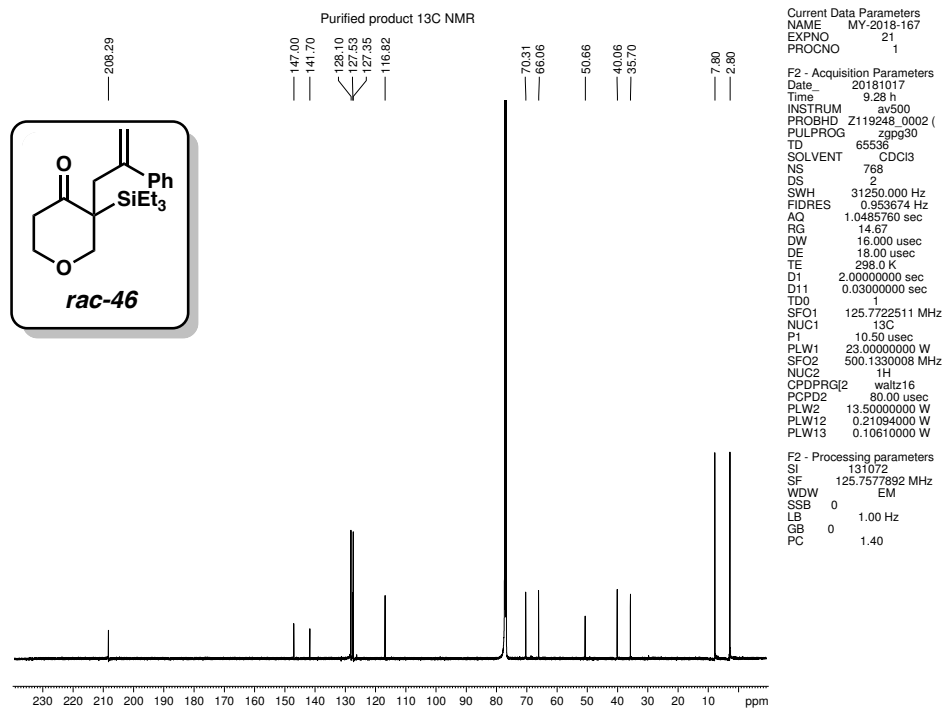
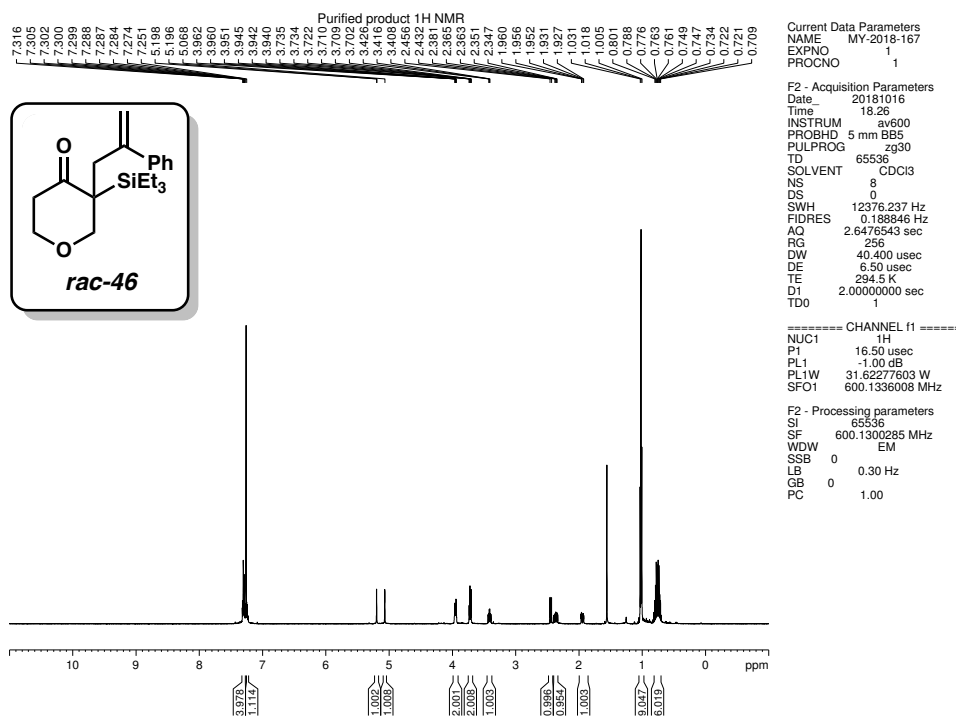


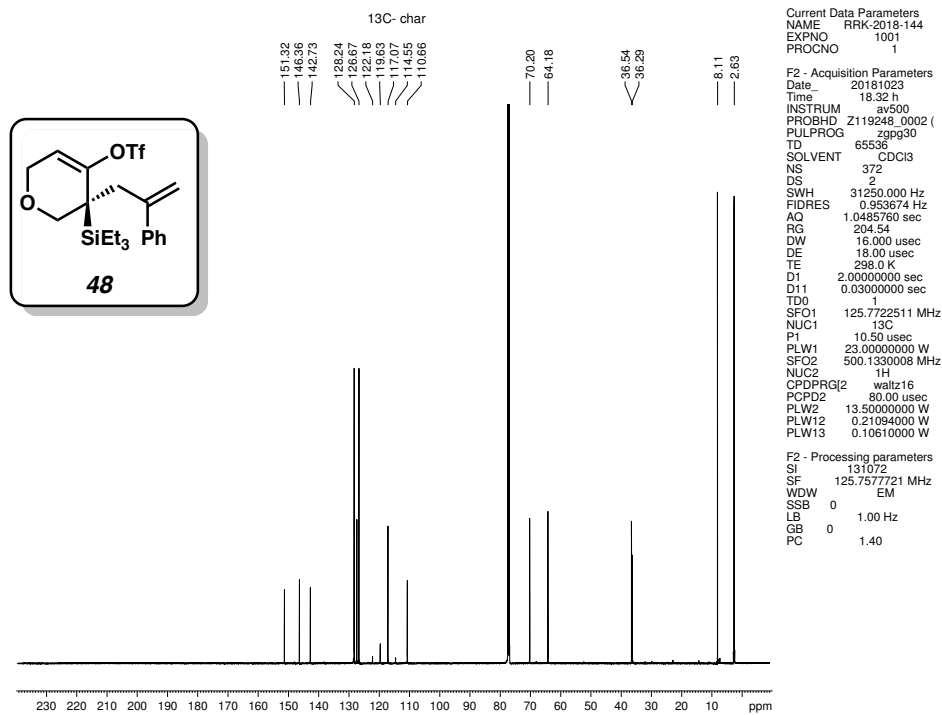
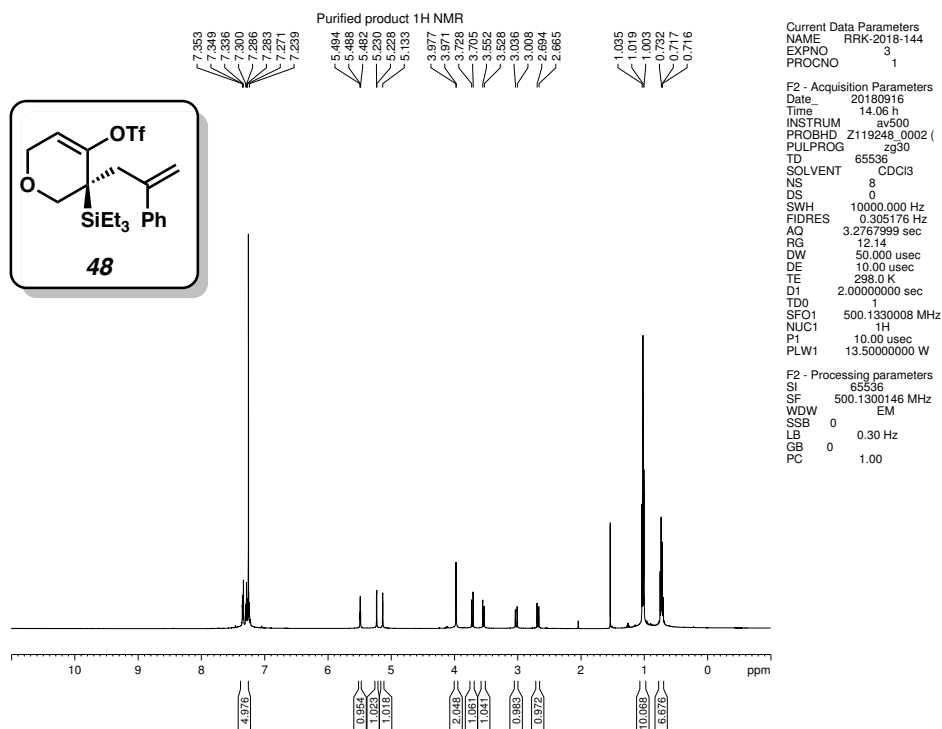


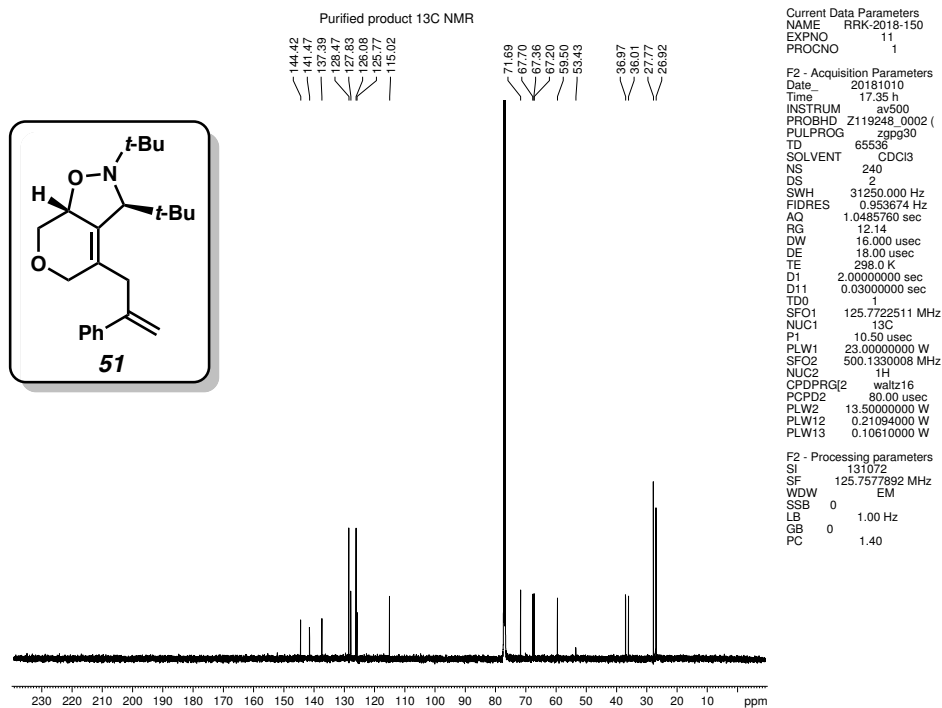
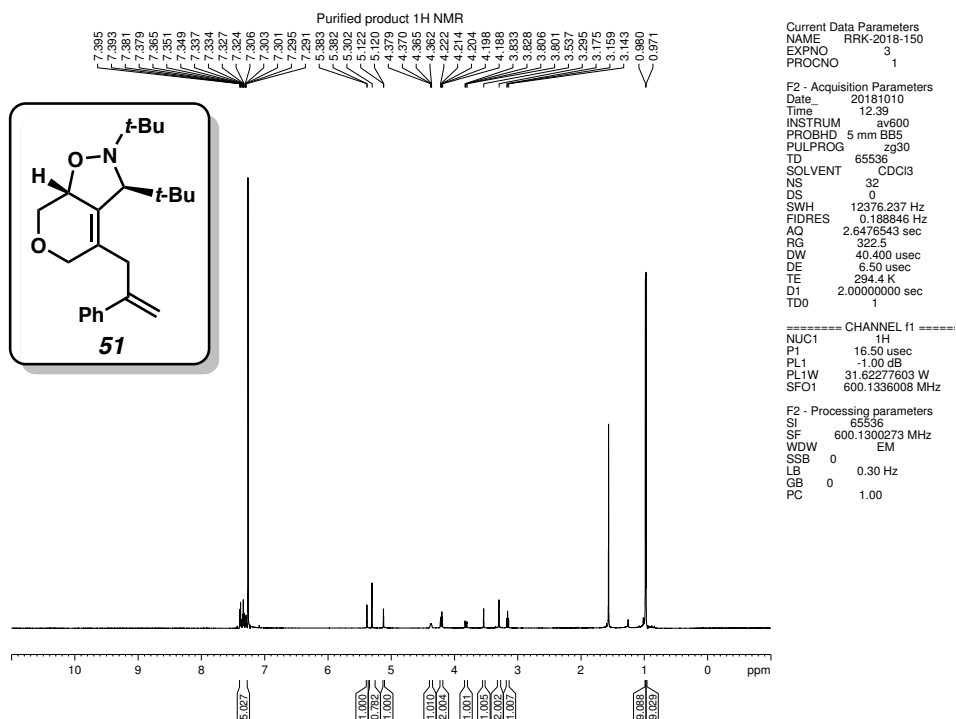


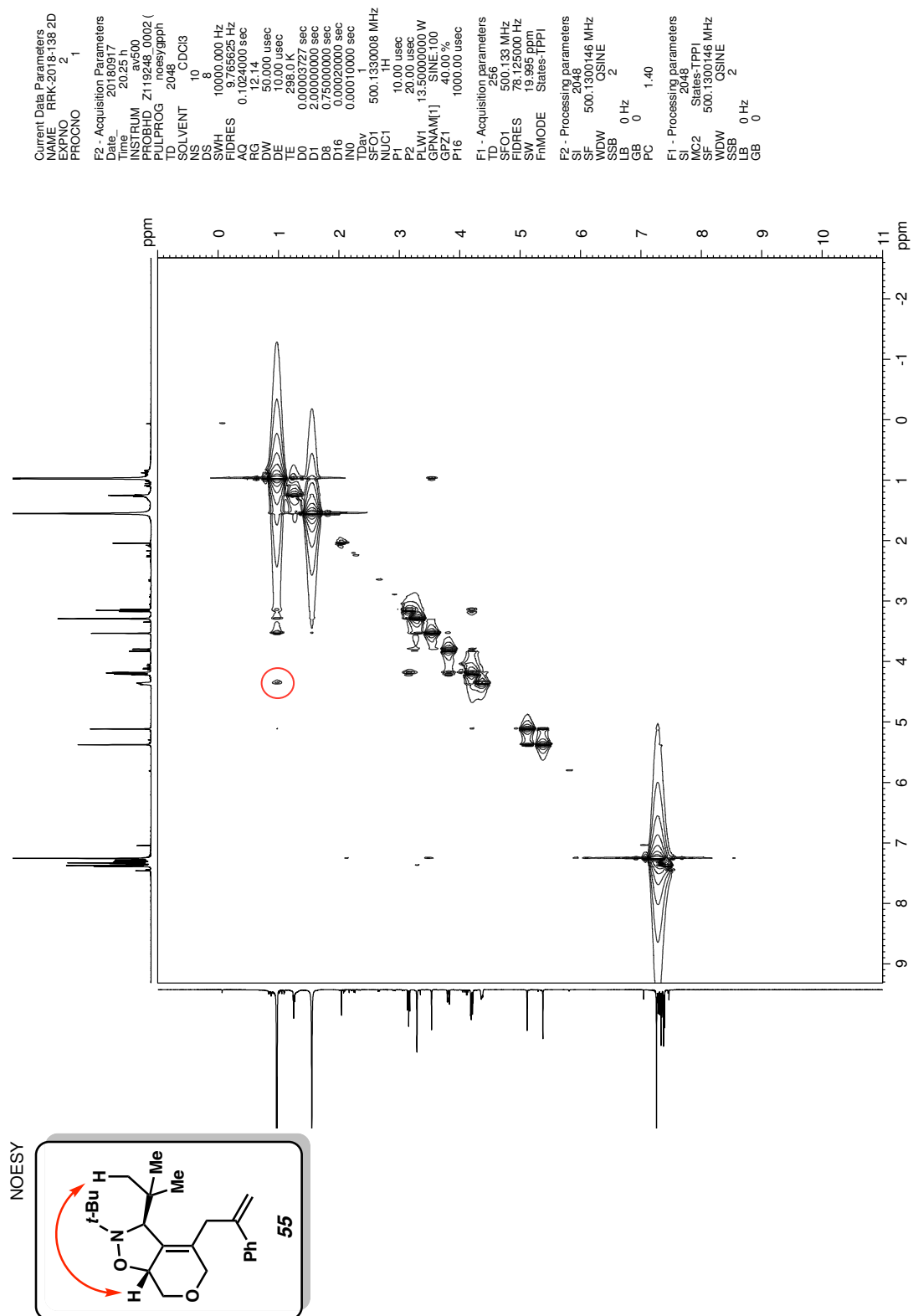




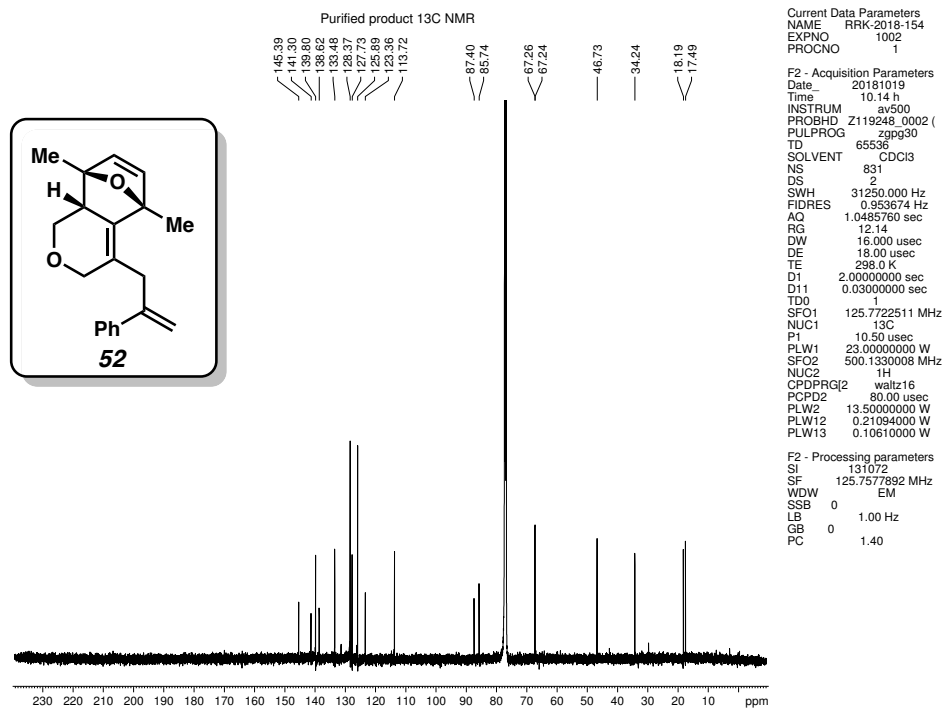
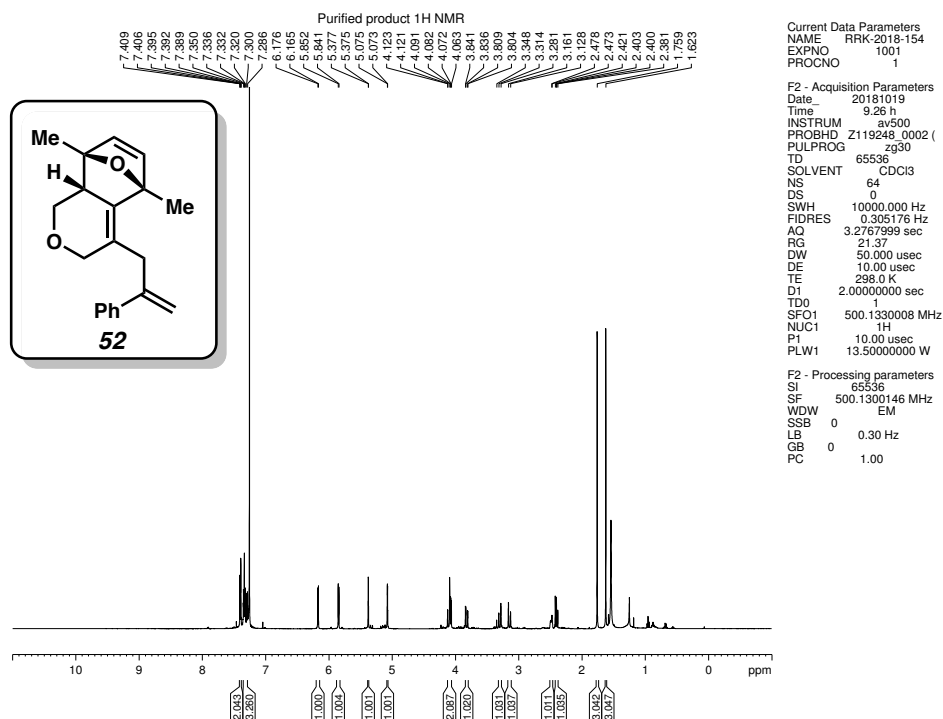


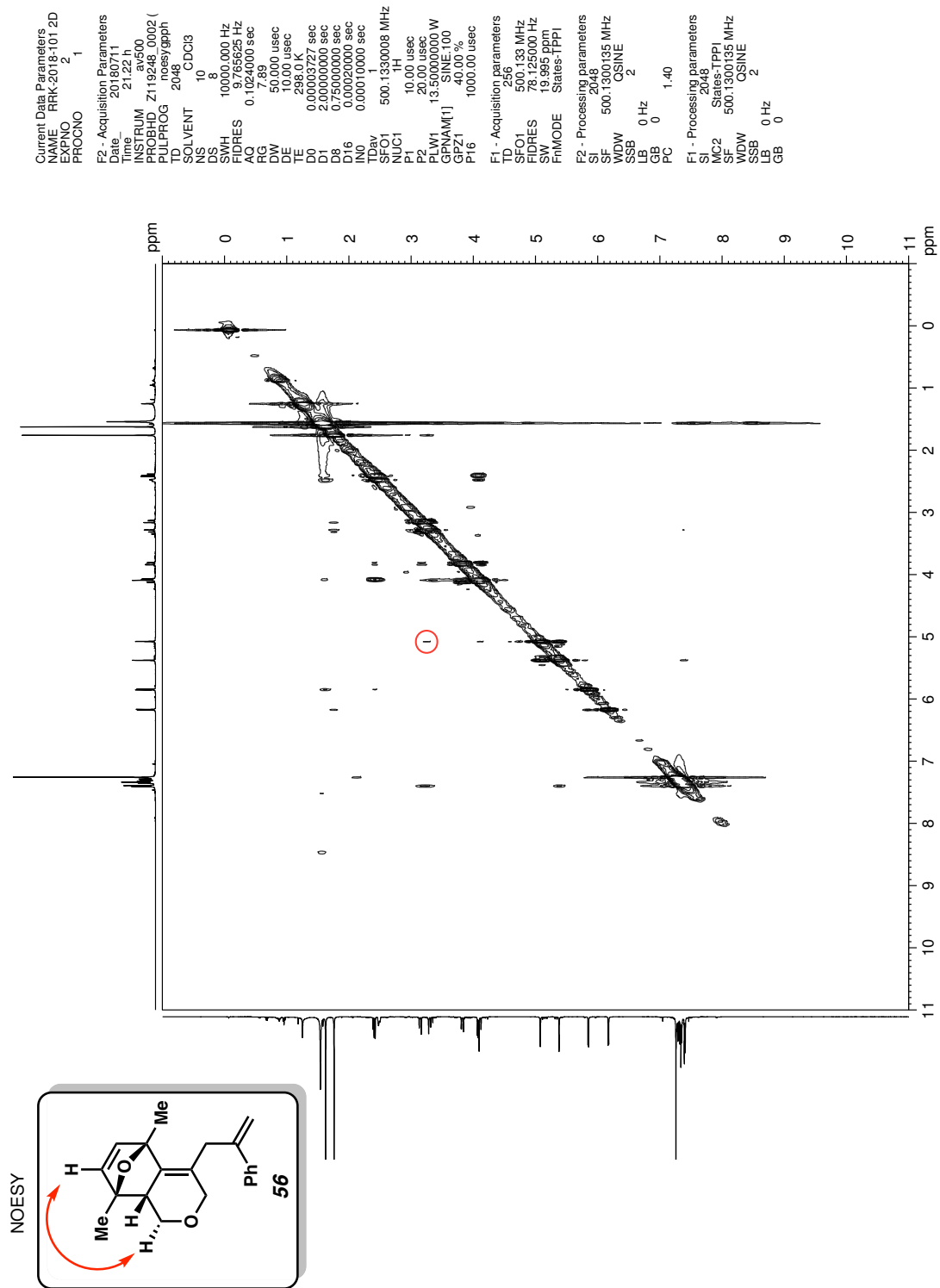












## Part II: Computational Methods

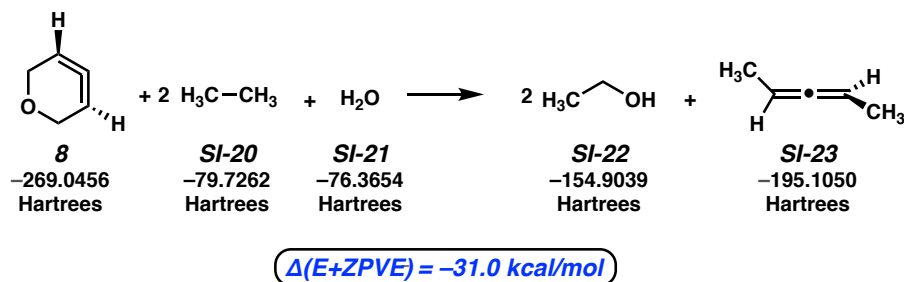
### Computational Details

All calculations were carried out with the Gaussian 09 package. Geometry optimizations were performed with  $\omega$ B97XD and 6-31G(d) basis set. Frequency analysis was conducted at the same level of theory to verify the stationary points to be minima or saddle points. Free energy corrections were calculated with and without Truhlar's quasiharmonic oscillator approximation.<sup>10</sup> Single-point energies and solvent effects in acetonitrile were computed with the 6-311+G(d,p) basis set and SMD solvation model.<sup>10</sup> Computed structures are illustrated with CYLview.<sup>11</sup>

### A. Complete Citation of Gaussian 09

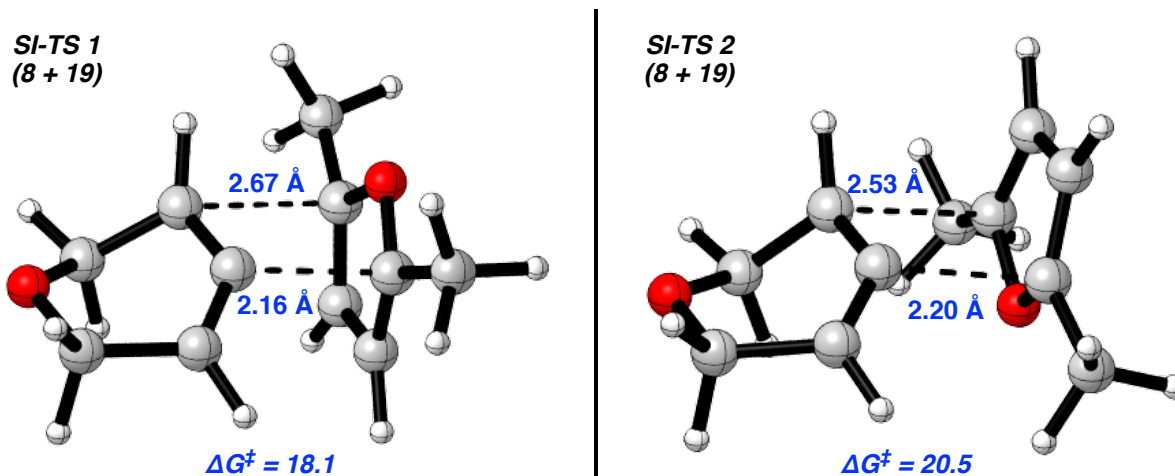
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### B. Strain Energy in 3,4-Oxacyclohexadiene



A homodesmotic equation at the  $\omega$ B97XD/6-31G(d)+ZPVE level of theory was used to estimate strain in 3,4-oxacyclohexadiene **8**. Molecular strain in 3,4-oxacyclohexadiene **8** was calculated relative to penta-2,3-diene (**SI-15**).

### C. Geometries of Diastereomeric Transition States



Transition states geometries for concerted cycloaddition of 3,4-oxacyclohexadiene **8** with dimethylfuran (**SI-16**) at the  $\omega$ B97XD/6-31G(d) level of theory. **SI-TS 1** leads to endo product (major diastereomer) while **SI-TS 2** leads to exo product (minor diastereomer). Endo and exo refer to the position of dimethylfuran (**SI-16**) relative to the additional  $\pi$  bond in 3,4-oxacyclohexadiene **8**.  $\Delta G^\ddagger$  values are provided ( $\omega$ B97XD/6-311+G(d,p)/SMD(MeCN)// $\omega$ B97XD/6-31G(d)). The reaction occurs with a notable preference for formation of endo product ( $\Delta\Delta G^\ddagger = 2.4$  kcal/mol).

### D. Energies and Cartesian Coordinates for Optimized Structures

**8**

C	-1.24674000	-0.57333100	-0.16257500
C	-1.12327600	0.91341500	0.18876500
C	0.08600700	1.36248600	-0.07564900
C	1.24937000	0.76182500	-0.23306100
C	1.11910400	-0.61060800	0.41350800
H	-1.86684900	1.38110200	0.82463900
H	-1.84708100	-1.01059600	0.64995900
H	-1.74890600	-0.77716500	-1.11281700
H	1.99450900	0.97944500	-0.99017200
H	1.96652800	-1.26520500	0.20070900

H	0.96600200	-0.54212500	1.49727300
O	0.00362700	-1.23602200	-0.23194000

Electronic energy ( $\omega$ B97XD/6-311+G(d,p)/SMD(MeCN)) = -269.226878421 Hartrees

Zero-point correction = 0.098770 Hartrees

Thermal correction to enthalpy = 0.104786 Hartrees

Thermal correction to Gibbs free energy = 0.070625 Hartrees

Quasiharmonic free energy correction = 0.070625 Hartrees

## SI-20

C	0.00000	0.00000	0.76352
H	-0.51001	0.88390	1.16085
H	-0.51048	-0.88363	1.16085
C	0.00000	0.00000	-0.76352
H	0.51001	0.88390	-1.16085
H	0.51048	-0.88363	-1.16085
H	-1.02049	-0.00027	-1.16085
H	1.02049	-0.00027	1.16085

Zero-point correction = 0.075745 Hartrees

Thermal correction to enthalpy = 0.080183 Hartrees

Thermal correction to Gibbs free energy = 0.054300 Hartrees

Sum of electronic and zero-point energies = -79.726239 Hartrees

Sum of electronic and thermal free energies = -79.747684 Hartrees

## SI-21

O	0.00000000	0.00000000	0.11835300
H	0.00000000	-0.75982300	-0.47341300
H	0.00000000	0.75982300	-0.47341300

Zero-point correction = 0.021663 Hartrees

Thermal correction to enthalpy = 0.025442 Hartrees

Thermal correction to Gibbs free energy = 0.004014 Hartrees

Sum of electronic and zero-point energies = -76.365400 Hartrees

Sum of electronic and thermal free energies = -76.383049 Hartrees

## SI-22

C	1.21220100	-0.23804600	-0.02145400
H	1.27565200	-0.96134700	0.80086000
H	1.27171200	-0.78838200	-0.96517700
H	2.07963300	0.42696600	0.05161300
C	-0.08746000	0.55385200	0.04686200
H	-0.13308800	1.12497000	0.98764200
H	-0.13020500	1.27850500	-0.77122400
O	-1.23362900	-0.26044600	-0.10945000

H	-1.24312300	-0.89198300	0.61943800
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Zero-point correction = 0.081357 Hartrees

Thermal correction to enthalpy = 0.086504 Hartrees

Thermal correction to Gibbs free energy = 0.056044 Hartrees

Sum of electronic and zero-point energies = -154.903918 Hartrees

Sum of electronic and thermal free energies = -154.929231 Hartrees

**SI-23**

C	-1.24593	0.42500	-0.39103
H	-1.53233	1.11346	-1.18552
C	0.00103	0.42443	0.00316
C	1.24770	0.41219	0.39710
H	1.54455	1.07911	1.20724
C	2.32360	-0.46493	-0.19107
C	-2.32704	-0.46771	0.18235
H	1.92918	-1.08347	-1.00123
H	3.14621	0.14154	-0.58765
H	2.74684	-1.12632	0.57413
H	-2.09267	-1.52653	0.03124
H	-2.45039	-0.30527	1.25798
H	-3.28755	-0.26641	-0.29927

Zero-point correction = 0.114035 Hartrees

Thermal correction to enthalpy = 0.120870 Hartrees

Thermal correction to Gibbs free energy = 0.084996 Hartrees

Sum of electronic and zero-point energies = -195.105045 Hartrees

Sum of electronic and thermal free energies = -195.134084 Hartrees

**19 (dimethylfuran)**

C	-1.10062400	-0.00470800	0.00004100
C	-0.71706500	1.29740800	-0.00025200
C	0.71706700	1.29740700	0.00006000
C	1.10062300	-0.00471000	0.00005200
O	-0.00000100	-0.80721700	-0.00020300
H	-1.37548700	2.15469400	-0.00042000
H	1.37549200	2.15469100	0.00014700
C	2.42341600	-0.68444500	0.00015600
H	2.54622400	-1.31905700	0.88483900
H	2.54636800	-1.31906000	-0.88450600
H	3.22063300	0.06276700	0.00022400
C	-2.42341600	-0.68444400	0.00010500
H	-3.22063500	0.06276600	-0.00005000
H	-2.54625500	-1.31920100	-0.88446900
H	-2.54633500	-1.31891500	0.88487600

Electronic energy ( $\omega$ B97XD/6-311+G(d,p)/SMD(MeCN)) = -308.653185 Hartrees

Zero-point correction = 0.127026 Hartrees

Thermal correction to enthalpy = 0.135217 Hartrees

Thermal correction to Gibbs free energy = 0.094751 Hartrees

Quasiharmonic free energy correction = 0.095992 Hartrees

### SI-TS 1 (Endo TS)

C	-3.09697200	0.53986500	0.08949300
C	-1.72490200	1.19375000	0.16339200
C	-0.73978900	0.47238900	-0.35074300
C	-0.72115400	-0.84428800	-0.64485900
C	-1.82221600	-1.51330600	0.13848900
C	1.26139500	1.20505200	-0.02795700
C	1.83661800	-0.89929500	0.10820000
C	1.24115600	0.86703000	1.32807100
C	1.56843800	-0.48951000	1.40092100
O	1.83315000	0.17071900	-0.71773600
H	-3.56915800	0.71581500	1.07102100
H	-3.74945400	0.97662800	-0.67491100
H	-1.99004000	-2.55380600	-0.14818000
H	-1.62636700	-1.46235800	1.21941500
H	0.91250500	1.51476100	2.12839500
H	1.55397900	-1.13047700	2.27124300
H	-0.38847700	-1.24903100	-1.59519300
H	-1.59926300	2.08697200	0.77041400
O	-3.05573100	-0.84722300	-0.17652800
C	2.36268600	-2.17793600	-0.44282200
C	1.30390200	2.54298400	-0.69062900
H	3.44754900	-2.12521100	-0.59328000
H	2.15096500	-2.99456400	0.25125200
H	1.89920300	-2.40941000	-1.40529700
H	2.30831900	2.97814400	-0.64227400
H	1.00628600	2.46175800	-1.73838300
H	0.60963000	3.22240700	-0.18943600

Electronic energy ( $\omega$ B97XD/6-311+G(d,p)/SMD(MeCN)) = -577.874242 Hartrees

Zero-point correction = 0.227431 Hartrees

Thermal correction to enthalpy = 0.240808 Hartrees

Thermal correction to Gibbs free energy = 0.188687 Hartrees

Quasiharmonic free energy correction = 0.189677 Hartrees

### SI-TS 2 (Exo TS)

C	1.69391300	1.30305400	-0.03890400
C	3.06127400	0.62432200	-0.06184600
C	1.76074100	-1.40882000	-0.18107600

C	0.71350700	-0.77499800	0.69939200
C	0.71501400	0.55747900	0.44412900
C	-1.91718400	0.80237900	1.16055900
C	-1.34207800	1.16635600	-0.06112500
C	-1.66289200	-0.98957100	-0.14049000
C	-2.09782500	-0.57607500	1.11331500
O	-1.42199300	0.09598800	-0.90790000
H	3.49701300	0.84836400	-1.04985300
H	3.74982300	1.00641200	0.70036000
H	1.51457900	-1.28143500	-1.24511200
H	1.92870700	-2.46775000	0.02777800
H	-2.06169900	1.46437000	2.00284000
H	-2.41623500	-1.23272100	1.91112800
H	0.52789900	-1.19348700	1.68285300
O	3.01143800	-0.77500900	0.12792000
H	1.58138800	2.24346900	-0.57139500
C	-1.21761600	2.50721200	-0.70306000
H	-2.18574500	2.86027200	-1.07503400
H	-0.84111000	3.23114900	0.02429100
H	-0.52180600	2.46445900	-1.54419100
C	-1.74103500	-2.30600600	-0.83144500
H	-1.68160300	-3.11271900	-0.09696800
H	-2.68372300	-2.41089500	-1.38191400
H	-0.91796400	-2.41931400	-1.54164000

Electronic energy ( $\omega$ B97XD/6-311+G(d,p)/SMD(MeCN)) = -577.871663 Hartrees

Zero-point correction = 0.228067 Hartrees

Thermal correction to enthalpy = 0.241220 Hartrees

Thermal correction to Gibbs free energy = 0.189701 Hartrees

Quasiharmonic free energy correction = 0.190847 Hartrees

## References

- <sup>11</sup> R. F. Ribeiro, A. V. Marenich, C. J. Cramer, D. G. Truhlar *J. Phys. Chem. B* **2011**, *115*, 14556.
- <sup>12</sup> A. V. Marenich, C. J. Cramer, D. G. Truhlar *J. Phys. Chem. B* **2009**, *113*, 6378–6396.
- <sup>13</sup> C. Y. Legault, CYLView, 1.0b; Université de Sherbrooke: Quebec, Montreal, Canada, <http://www.cylview.org> (2009).